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THE MOLECULAR WEIGHT OF ALUMINIUM COMPOUNDS.

BY ELMER P. KOHLER.

The molecular weight of aluminium compounds has been the subject of investigations by Deville and Troost,[1] Odling and Buckton,[2] V. Meyer and C. Meyer,[3] Nilson and Pettersson,[4] Friedel and Crafts,[5] Roux and Louise,[6] Combes,[7] and Werner and Schmujlow.[8] All of the earlier results, obtained by applying vapor-density methods to aluminium halides, lead to the general formula Al_2X_6 for these salts. All the later results—obtained partly by vapor-density and partly by newer methods—lead to the general formula AlX_3 for all classes of aluminium compounds. The last two investigations, in particular, have appeared so conclusive that the double formulas have been more or less reluctantly abandoned. Combes determined the vapor-density of aluminium acetylacetone and obtained results that agree perfectly with the formula $Al(C_5H_7O_2)_3$, showing that in compounds of this type aluminium is unquestionably trivalent. Werner and Schmujlow de-

[1] Ann. chim. phys. [3], **58**, 257.
[2] Phil. Mag. [4], **29**, 316.
[3] Ber. d. chem. Ges., **12**, 1199.
[4] Ztschr. phys. Chem., **1**, 456.
[5] Compt. rend., **106**, 73; **106**, 602; **107**, 600.
[6] *Ibid.*, **106**, 1764.
[7] *Ibid.*, **108**, 405.
[8] Ztschr. anorg. Chem., **15**, 24.

termined the molecular weight of aluminium chloride by the boiling-point method, using pyridine as solvent. Their results agree closely with the formula $AlCl_3$.

The investigation described in this paper was undertaken as a result of some observations made while studying the mechanism of organic reactions, that are induced by aluminium halides. The aim was the determination of the molecular weight of aluminium halides, as well as that of their addition- and reaction-produets, as nearly as possible under the same conditions as those under which they are used and formed in organic reactions; namely, dissolved in some low-boiling, indifferent medium.

The substances studied were:

I. Organic compounds like aluminium acetylacetone.

II. Aluminium halides.

III. Compounds formed by the addition of aluminium halides to a number of different classes of organic and inorganic compounds.

Nearly all the determinations were made by the boiling-point method, with carbon disulphide as solvent; but at the end of the paper some experiments are described in which nitrobenzene was used as solvent for determinations by the freezing-point method. These were made to determine the behavior of the addition-products, above referred to, in the presence of a large excess of one of the components. They show the relation between the results described in this paper and those obtained by Werner and Schmujlow.

I. ORGANIC ALUMINIUM COMPOUNDS.

Aluminium Acetylacetone.

Solvent: Carbon disulphide. $K = 2,370$.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	39.4195	1.2340	0.194	329
2	"	1.7848	0.330	326
3	"	2.3458	0.425	331
			Mean,	328
			Calculated for $Al(C_5H_7O_2)_3$,	324.3

Aluminininium Acetoacetic Ester.

Solvent: Carbon disulphide. K = 2,370.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.1505	1.5400	0.220	413
2	"	2.1825	0.306	421
3	"	2.8050	0.396	418
			Mean,	417
			Calculated for $Al(C_6H_9O_3)_3$,	414.4

These determinations presented no difficulties, and the results, as expected, fully confirm those of Combes.

II. ALUMINIUM HALIDES.

Aluminium chloride is insoluble in carbon disulphide, hence its molecular weight could not be determined directly. An indirect determination is given under the addition-products.

Aluminium bromide was made by Mallet's method,[1] from pure bromine and metallic aluminium. To avoid the troublesome distillations, necessary to free it from bromides of carbon, silicon, and iron, the following method of purification was adopted: A piece of Jena-glass tubing 3 meters long was constricted at three points, and bent, at the constrictions, into a flattened W. One of the ends was drawn into a capillary and connected with a phosphorus pentoxide drying-tube which, in turn, was connected with a pump. Aluminium wire that had been heated to a low red heat in a current of hydrogen was placed in the limb next to the other end, that connected with the retort in which the bromide had been prepared, and the latter distilled into the tube. This end of the tube was then sealed off. The limb holding the bromide and wire was wrapped with thin asbestos paper and placed in a furnace in such a position that the second limb served as a reflux condenser. The bromide was boiled until colorless, when the other end of the tube was sealed off, the position of the tube changed, and the bromide distilled from the first into the second limb. The first limb was then sealed off at the constriction, the position of the tube changed; and the distillation repeated, etc.

[1] Trans. Roy. Soc. (1880), 1003; and This JOURNAL, 3, 77.

The second distillation left a slight residue of oxybromide; the third no residue at all. The bromide was thus obtained sealed up in the fourth limb. To get it into convenient form for use, it was melted into a layer of uniform thickness throughout the length of the tube. By hitting the tube sharply with a block of wood the layer could be readily broken up into lumps of any desired size. In this way there is no difficulty either in preparing or manipulating the bromide.

The principal difficulty met with in this part of the work consisted in getting and keeping carbon disulphide sufficiently free from water. After a most careful purification it was repeatedly distilled from phosphorus pentoxide; but though used immediately after distillation, enough water was invariably present to cause errors of from 50 to 100 in the molecular weight. The difficulty which has been experienced by others[1] working with such sensitive substances, is due to the adsorption of water by the apparatus. To remove this water, the weighed molecular-weight apparatus was filled with dry carbon disulphide, and a considerable quantity of the latter distilled off, the vapor sweeping freely through the condenser. The condenser was then capped with phosphorus pentoxide tubes that were ground on, the apparatus closed with a ground glass stopper, and weighed with the thermometer in place.

Pure dry carbon disulphide dissolves aluminium bromide without any indication of chemical action. The solution is clear and colorless; its boiling-point remains constant during protracted boiling; and, if the disulphide is allowed to evaporate at ordinary temperatures, the pure bromide crystallizes out in large, lustrous rhombohedra. These are far less sensitive to atmospheric moisture than the lumps of the fused salt. An analysis of the crystals gave 10.02 per cent aluminium and 89.72 per cent bromine, instead of the calculated 10.15 per cent aluminium and 89.85 per cent bromine.

Molecular Weight of Aluminium Bromide.

Solvent: Carbon disulphide. K = 2,370.

[1] Rosenheim and Woge: Ztschr. anorg. Chem., **15**, 283.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.1510	0.6110	0.067	539
2	"	1.3660	0.149	542
3	"	2.2895	0.250	540
4	"	3.1000	0.340	538
5	"	3.7410	0.405	545
6	"	4.3840	0.479	540
			Mean,	540.6
			Calculated for Al_2Br_6,	534

Aluminium Iodide.

The iodide was prepared by the method of Gustavson,[1] and purified in exactly the same way as the bromide.

Solvent: Carbon disulphide. K = 2,370.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.4550	1.0120	0.072	824
2	"	1.5175	0.110	808
3	"	2.2380	0.160	819
4	"	3.1080	0.222	822
5	"	4.3200	0.310	826
			Mean,	822.25
			Calculated for Al_2I_6,	815.30

III. ADDITION-PRODUCTS.

Aluminium bromide, like aluminium chloride, combines directly with acid chlorides, ketones, esters, nitro compounds, and tertiary amines. The compounds obtained with the bromide are invariably more easily soluble in carbon disulphide than those obtained with the chloride. It is, therefore, easier to get them in a form in which it is possible to use them for molecular weight work. They are, at best, extremely difficult to manipulate, and only very few gave satisfactory results. With these, however, it was possible to prove that for the purpose of this investigation it is not at all necessary to isolate the substances. They can just as well be made in the apparatus in which their molecular weight is to be determined.

[1] Ann. Chem. (Liebig), **172**, 173.

Benzene Sulphonchloride and Aluminium Bromide.

Slightly more than 2 molecules of pure benzene sulphonchloride were added to 1 molecule of aluminium bromide dissolved in a large amount of carbon disulphide. The flask was closed with a phosphorus pentoxide tube and the disulphide allowed to evaporate slowly through the tube. In the course of a week the product began to separate in large, colorless tables. The solution was removed in a current of dry air, the crystals washed with dry disulphide, dried in a current of dry air, and used without further purification. A halogen determination gave the following results:

I. 0.3245 gram substance gave 0.5152 gram silver halide.
II. 0.4105 gram substance gave 0.6530 gram silver halide.

	Calculated for $(AlBr_3.C_6H_5SO_2Cl)x$.	Found. I.	II.
Cl, Br	62.07	61.8	61.9

Molecular Weight of $(AlBr_3.C_6H_5SO_2Cl)_x$.

Solvent: Carbon disulphide. K = 2,370.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.1110	1.0030	0.086	899
2	"	1.9230	0.128	887
3	"	3.1255	0.210	879
4	"	3.7110	0.244	898
			Mean,	890.75
		Calculated for $Al_2Br_6.2C_6H_5SO_2Cl$,		887.08

Nitrobenzene and Aluminium Bromide.

Gatterman[1] found that aluminium chloride combines with nitrobenzene to form a crystalline addition-product of the composition $AlCl_3.C_6H_5NO_2$. The corresponding aluminium bromide compound crystallizes well, at low temperatures, forming large yellow prisms considerably less sensitive to atmospheric moisture than the analogous addition-products with acid chlorides. The substance was washed with dry carbon disulphide and dried in a current of air.

[1] Ber. d. chem. Ges., **12**, 2719.

Molecular Weight of $(AlBr_3.C_6H_5NO_2)_x$.

Solvent: Carbon disulphide. K = 2,370.

	Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
1	40.2020	0.8510	0.064	784
2	"	1.8200	0.135	794
3	"	2.3840	0.178	789
4	"	2.9630	0.220	794
			Mean,	790.25
			Calculated for $Al_2Br_6.2C_6H_5NO_2$,	780.14

According to these results, 1 molecule of aluminium bromide combines with 2 molecules of other substances to form 1 molecule of product:

$$Al_2Br_6 + 2C_6H_5SO_2Cl = Al_2Br_6.2C_6H_5SO_2Cl,$$
$$Al_2Br_6 + 2C_6H_5NO_2 = Al_2Br_6.2C_6H_5NO_2.$$

If these equations are correct, then the addition of sulphonchloride or nitro compound to a solution of aluminium bromide of known boiling-point should not affect the boiling-point so long as the bromide is in excess; while the addition of the bromide to a solution of benzene sulphonchloride or nitrobenzene should immediately lower the boiling-point, and the lowering should be proportional to the gram-molecular amounts of bromide added. The experimental results are as follows:

Effect of Adding Benzene Sulphonchloride to a Solution of Aluminium Bromide.

Solvent: Carbon disulphide. K = 2,370.

	Solvent. Grams.	Bromide. Grams.	Sulphonchloride. Grams.	Boiling-point.	Change in boiling-point.
1	39.7150	....	....	2.572	....
2	"	1.7730	....	2.770	0.198
3	"	"	0.2335	2.770	0.000
4	"	"	0.6980	2.770	0.000
5	"	"	1.1840	2.810	0.040

The weight of sulphonchloride equivalent to 1.7730 grams aluminium bromide is 1.1749 grams; the amount added is 1.1840 grams; the elevation of the boiling-point calculated

for the difference, assuming—what is only approximately true—that the constant for the solution is the same as that for the pure solvent, is 0.045; the elevation found is 0.040.

Effect of Adding Aluminium Bromide to a Solution of Benzene Sulphonchloride.

	Solvent. Grams.	Sulphonchloride. Grams.	Bromide. Grams.	Boiling-point.	Change in boiling-point.
1	41.8860	....	....	2.590	....
2	"	2.5150	....	3.394	+0.804
3	"	"	0.5050	3.342	—0.052
4	"	"	1.3800	3.247	—0.142
5	"	"	2.5950	3.118	—0.275

The molecular weight of aluminum bromide calculated from these lowerings, assuming K = 2,370 is as follows:

	Solvent. Grams.	Bromide. Grams.	Lowering of boiling-point.	Molecular weight.
1	41.8860	0.5050	0.052	560
2	"	1.3800	0.142	548
3	"	2.5950	0.275	536
		Calculated for Al_2Br_6,		534

No better proof of the formula Al_2Br_6 seems possible. No other assumption would explain these results. It will be observed that the error introduced by the presence of the sulphonchloride is small in comparison with the normal error of these determinations, which is unavoidably large, partly owing to the sensitiveness of the substances and partly to their great molecular weight. Knowing that aluminium chloride combines with nitrobenzene to form a compound $(AlCl_3.C_6H_5NO_2)_x$, it is possible to determine whether the formula of the chloride is analogous to that of the bromide or not.

Aluminium Chloride and Nitrobenzene.

Solvent: Carbon disulphide. K = 2,370.

	Solvent. Grams.	Nitrobenzene. Grams.	Chloride. Grams.	Lowering of boiling-point.	Molecular weight.
1	40.2250	2.1310	0.8250	0.170	284
2	"	"	1.4355	0.308	275
3	"	"	2.0310	0.444	270
				Mean,	276.33
				Calculated for Al_2Cl_6,	266.9

The facts established up to this point supply an elegant method for determining what happens when an aluminium halide is brought in contact with a given substance in an indifferent medium. It is sufficient, for this purpose, to prepare a solution of aluminium bromide, of known concentration and boiling-point, to add to this successive portions of the substance under investigation, until it is present in excess, and then add a fresh portion of aluminium bromide. The thermometer readings after each addition of material, give an accurate account of what goes on in the solution. The following results were obtained in this way:

Aluminium Bromide and Benzoyl Chloride.

The calculations are based on the equation

$$Al_2Br_6 + 2C_6H_5COCl = Al_2Br_6.2C_6H_5COCl.$$

Solvent: Carbon disulphide. $K = 2,370$.

	Solvent. Grams.	Bromide. Grams.	Chloride. Grams.	Change in boiling-point.	Calculated change in boiling-point.
1	38.1500	1.7140	....	+0.020	+0.0215
2	"	"	0.3370	0.000	0.000
3	"	"	0.9460	0.000	0.000
4	"	"	1.2380	+0.128	+0.130
5	"	2.2670	"	−0.053	−0.054

Aluminium Bromide and Benzophenone.

The calculations are based on the equation,

$$Al_2Br_6 + 2C_6H_5COC_6H_5 = Al_2Br_6.2C_6H_5COC_6H_5.$$

	Solvent. Grams.	Bromide. Grams.	Ketone. Grams.	Change in boiling-point.	Calculated change in boiling-point.
1	40.1510	1.1010	....	+0.118	+0.121
2	"	"	0.4117	0.000	0.000
3	"	"	1.3290	+0.211	+0.213
4	"	1.6120	"	−0.054	−0.057

Aluminium Bromide and Phosphorus Oxychloride.

The calculations are based on the equation,

$$Al_2Br_6 + 2POCl_3 = Al_2Br_6.2POCl_3.$$

	Solvent. Grams.	Bromide. Grams.	Oxychloride. Grams.	Change in boiling-point.	Calculated change in boiling-point.
1	40.2150	1.3520	....	+0.147	+0.150
2	"	"	0.6772	0.000	0.000
3	"	"	1.2282	0.172	+0.173
4	"	1.8070	"	—0.047	—0.050

Aluminium Bromide and Dibrombenzene (p).

The Friedel and Crafts reaction is not applicable to dihalogen compounds. The experiment was made to determine whether this is due to a combination of the halogen compound with the aluminium halide. The results show that this is not the case. The calculations are based on the assumption that both substances are present unchanged:

	Solvent. Grams.	Bromide. Grams.	Dibrombenzene. Grams.	Rise in boiling-point.	Molecular weight.
1	40.6650	1.7000	....	0.186	533
2	"	"	0.5860	0.140	244
3	"	"	1.4400	0.340	246
4	"	"	2.2040	0.540	240
5	"	2.8050	"	0.120	540
			Calculated for Al_2Br_6,		534
			Calculated for $C_6H_4Br_2$		236

Of other substances examined, acetophenone, benzene sulphonacetone, and ethyl benzoate, form addition-products with aluminium halides, and behave like benzophenone. Benzene and naphthalene give results like those of dibrombenzene, but they slowly react to form insoluble compounds. Pyridine and quinoline form crystalline addition-products insoluble in carbon disulphide.

The results thus far given show conclusively that in an indifferent medium the aluminium halides form addition-products that are not measurably dissociated. The results are quite different when a large excess of one of the components is present. It was shown, above, that in carbon disulphide aluminium bromide combines with nitrobenzene to form a compound of the formula $Al_2Br_6.2C_6H_5NO_2$. If this compound, or aluminium bromide itself, is dissolved in nitrobenzene and the lowering of the freezing-point of the latter measured, the result leads to a much simpler formula.

Aluminium Bromide in Nitrobenzene.

K = 7,070.

	Nitrobenzene. Grams.	Bromide. Grams.	Lowering of freezing-point.	Molecular weight.
1	15.2470	1.2530	2.11	275.5
2	"	1.9040	3.20	276.0
3	"	2.4250	4.08	277.0
			Mean,	276.17
			Calculated for $AlBr_3$,	267

Aluminium Chloride in Nitrobenzene.

K = 7,070.

	Nitrobenzene. Grams.	Chloride. Grams.	Lowering of freezing-point.	Molecular weight.
1	19.7640	0.1893	0.520	130.4
2	"	0.5953	1.675	127.5
3	"	0.8923	2.500	131.0
			Mean,	129.63
			Calculated for $AlCl_3$,	133.4

The results are exactly like those obtained in pyridine solution. As a mean of six determinations of the molecular weight of aluminium chloride in pyridine, Werner and Schmujlow obtained the value 129.6, and Werner concludes that $AlCl_3$ is the only formula permissible. The conclusion is not justified. Pyridine combines with aluminium chloride to form a well crystallized compound, and there is no experimental evidence that molecular weight determinations, made in solvents that combine with the substance under investigation, are trustworthy. In aqueous solutions they are not, and my results show that they are equally unreliable in this case. Between the results in carbon disulphide and those in nitrobenzene or pyridine, it is easy to decide by the aid of the following considerations: In the absence of any solvent benzoyl chloride combines with aluminium bromide to form a well crystallized compound which, as shown by analysis, has the composition $(AlBr_3.C_6H_5COCl)_x$. The molecular weight must, therefore, correspond to some multi-

ple of this formula. The determination in carbon disulphide gave a value corresponding to the double formula

$$(AlBr_3.C_6H_5COCl)_2$$

—a possible value. The determination in nitrobenzene gives an impossible value:

$$(AlBr_3.C_6H_5COCl)_x.$$

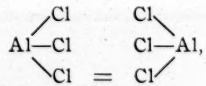
Solvent: Nitrobenzene. $K = 7{,}070$.

	Solvent. Grams.	Substance. Grams.	Lowering of freezing-point.	Molecular weight.
1	20.2500	0.5820	0.424	371
2	"	1.0105	0.952	370
3	"	1.8200	1.710	371

Calculated for $(AlBr_3.C_6H_5COCl)_x$, $(407.5)_x$.

It is evident from these results that nearly all the values for inorganic salts obtained by Werner and his pupils will need redetermination, since they purposely selected solvents that combine with salts and in many cases proved combination by isolating the products. The same is true of the determinations made by Lespeau[1] in ether, and those by Rosenheim and Woge[2] in pyridine.

The principal objections to the double formulas for the aluminium halides have been based on the assumption that these formulas imply quadrivalent aluminium.[3] To avoid this Traube[4] assumed that these salts are derived from an hexavalent complex of two aluminium atoms, $[Al{\equiv}Al]^{VI}$. Neither of these assumptions is necessary. The aluminium halides behave like typical double halides with the formula $Al^{III}Cl_3.Cl_3Al^{III}$ or the formula $(Al^{III}X_6)Al^{III}$. Their behavior in nitrobenzene and pyridine, moreover, makes it fairly certain that no double molecules are present in aqueous solution. The hydrous salt that crystallizes out of aqueous solutions is probably $AlCl_3.6H_2O$. The anhydrous salt is probably



[1] Bull. Soc. Chim. [3], **17**, 934.
[2] Ztschr. anorg. Chem., **15**, 283.
[3] Erdman: Lehrbuch d. anorg. Chem., 587.
[4] Ber. d. chem. Ges., **25**, 1716.

a double halide in harmony with Remsen's law.[1] The formula expresses the molecular weight, the power of direct addition, and the ease with which the substance is dissociated at higher temperatures and in solution. In any case I believe that the matter can be reached by experiment and the work will be continued in this direction and extended to include the compounds of iron.

BRYN MAWR COLLEGE,
CHEMICAL LABORATORY.

THE HYDROLYSIS OF ACID AMIDES.

BY EMMET REID.

In a previous article[2] I have given the results of a number of experiments on the rate of hydrolysis of the three nitrobenzamides both with acids and with alkalies, and of a number of other amides with hydrochloric acid. In the present work several other amides have been tried with hydrochloric acid, and all the amides available have been hydrolyzed with barium hydrate. It has seemed desirable to obtain additional measurements on some of the amides previously studied.

Preparation of Material.

For the amides previously worked upon, the same preparations have been used.

o-Phenoxybenzamide was readily made from *o*-phenoxybenzoic acid obtained from salol. 90 grams salol gave 22 grams *o*-phenoxybenzoic acid, and this with 22 grams phosphorus pentachloride yielded 13 grams of the amide. This required about 5 liters of boiling water for its solution, from which 10 grams of pearly crystals were obtained on cooling. The amide melted at 130° (corr.). The melting-point given in the literature is 128°.5–129° C. *o*-Brombenzamide was prepared from the *o*-brombenzoic acid obtained by extracting with hot water the mixture of brombenzoic acids resulting from the oxidation of liquid bromtoluene with potassium permanganate. The amide melted at 155°.6 (corr.), the melting-point given

[1] This formula is essentially the same as that used by Remsen (This JOURNAL, **11**, 316) to account for the peculiar results obtained in the determination of the vapor-density of aluminium chloride.

[2] This JOURNAL, **21**, 284.

in the literature being 155°–156°. *p*-Methoxybenzamide was made from anisic acid prepared by oxidizing *p*-methoxytoluene obtained according to Alleman's directions.[1]

p-Ethoxybenzamide was made from *p*-ethoxybenzoic acid similarly prepared.

o-Dimethylamidobenzamide was made by heating in a sealed tube *o*-amidobenzamide with methyl iodide. These three amides were identified by their melting-points but, I am sorry to say, the record has been lost.

Experiments with Hydrochloric Acid.

These form a continuation of the work already published, the methods of work being the same. That is, the required amount of amide was weighed out in a light weighing-bottle and dropped into a flask containing 600 cc. of hydrochloric acid of the proper strength. This flask had been for some time in a vigorously boiling water-bath. At intervals of thirty minutes samples were taken out, diluted with a known amount of water, cooled and measured, and the ammonia present determined by distilling with magnesium hydroxide into a standard acid. *o*-Phenoxybenzamide gave much trouble on account of its slight solubility, even in hot water. For this reason only half the usual concentration could be used. This increased the analytical difficulties. The second series is better than the first.

The columns of figures correspond to those in the previous article. The first gives time in minutes; the second the number of cubic centimeters of standard acid neutralized by the ammonia distilled from the sample. The third is the volume of the sample, while the fourth is the number of cubic centimeters of standard acid that would have been neutralized by the ammonia had all the amide in the sample been decomposed. The next is derived from these and gives the percentage of amide hydrolyzed. A is the concentration of the acid and B that of the amide. The eighth column contains the value of $K = \frac{2.3025}{(A-B)t} \log \frac{(A-x)B}{(B-x)A}$. The last column

[1] Dissertation, Johns Hopkins University, 1897, p. 8.

gives the same value corrected for the expansion of water from the room temperature at which the titrations and other measurements were made to the temperature of boiling water. This rise in temperature decreases the factor $A—B$ by about 4 per cent, and hence increases the value of K by the same amount. At the same time a correction has been applied for the variation of the boiling-point due to the variation of barometric pressure. In this the temperature curve found to hold for *m*-nitrobenzamide with caustic soda is assumed to hold. As the differences in temperature are only several tenths of a degree, at most, and the correction is small this seems allowable. In a few of the experiments this temperature correction is not applied owing to lack of data.

Results.

SERIES I.

HCl = A = 0.5646, B = 0.02013 N, $A—B$ = 0.5445, A/B = 28.05. B. p. water 99°.85 C.

o-Phenoxybenzamide, 2.379 Grams.

t.	Changed.	Volume of sample.	Equivalent of sample.	Per cent changed.	$A-x$.	$B-x$.	K.	K (cor.).
30	1.11	65.5	9.20	12.1	2793	87.9	0.00763	(0.00700)
60	1.72	64.2	9.01	19.9	2785	80.1	0.00657	0.00688
90	2.15	64.9	9.11	23.6	2781	76.4	0.00532	0.00557
120	2.42	54.0	7.58	31.9	2773	68.1	0.00570	0.00597
150	2.68	56.3	7.81	34.3	2771	65.7	0.00496	0.00518
180	3.80	67.1	9.42	40.4	2765	59.6	0.00513	0.00537
210	2.79	46.0	6.46	43.2	2762	56.8	0.00481	0.00503
240	6.60	94.7	13.30	49.7	2755	50.3	0.00512	0.00536

Series II.

HCl $= A = 0.5631$, $B = 0.02013$, $A - B = 0.5430$, $A/B = 27.97$. Temp. 99°.74 C.

o-Phenoxybenzamide, 2.379 Grams.

t.	Changed.	Volume of sample.	Equivalent of sample.	Per cent changed	x.	$A-x$.	$B-x$.	K.	K (cor.).
30	0.80	66.3	9.31	8.6	2789	91.4		0.00534	0.00562
60	1.52	64.6	9.07	16.7	2781	83.3		0.00543	0.00572
90	2.06	65.1	9.14	22.5	2775	77.5		0.00505	0.00532
120	3.02	70.4	9.89	30.5	2767	69.5		0.00542	0.00570
150	3.92	76.3	10.71	36.6	2760	63.4		0.00540	0.00568
180	4.80	83.8	11.77	40.8	2756	59.2		0.00522	0.00549
210	5.24	77.1	10.83	48.4	2749	51.6		0.00565	0.00595
240	5.96	80.2	11.26	52.9	2744	47.1		0.00563	0.00593

$B = 0.04081$, $A - B = 0.5223$, $A/B = 12.80$.

o-Dimethylamidobenzamide, 4.008 Grams.

30	0.29	64.1	18.01	1.7	1278	98.3	0.00098	0.00103
60	0.89	73.8	20.73	4.2	1276	95.8	0.00124	0.00130
90	0.90	63.6	17.85	4.9	1275	95.1	0.00098	0.00103
120	1.44	67.5	18.96	7.4	1273	92.6	0.00113	0.00118
150	1.80	66.6	18.71	9.4	1271	90.6	0.00117	0.00123
180	2.31	72.4	20.34	11.1	1269	88.8	0.00117	0.00123
210	2.91	81.7	22.95	12.4	1267	87.6	0.00115	0.00121
240	3.64	91.2	25.61	13.7	1266	86.3	0.00112	0.00118

Series III.

HCl $= A = 0.5617$, $B = 0.04026$, $A - B = 0.5214$, $A/B = 13.95$. Temp. 100°.14 C.

p-Methoxybenzamide, 3.033 Grams.

30	3.38	65.9	18.51	18.3	1377	81.7	0.0121	0.0125
60	5.78	59.4	16.68	34.6	1360	65.4	0.0128	0.0132
90	8.43	65.9	18.51	45.5	1350	54.5	0.0123	0.0127
120	11.44	73.1	20.53	55.7	1339	44.3	0.0124	0.0128
150	11.35	63.0	17.70	64.1	1331	35.9	0.0125	0.0129
180	13.91	68.0	19.10	72.8	1322	27.2	0.0133	0.0137
210	20.08	91.2	25.61	78.5	1317	21.5	0.0135	0.0139

SERIES III (*continued*).

p-Ethoxybenzamide, 3.313 Grams in 500 cc.

t.	Changed.	Vol. of sample.	Equiv. of sample.	Per cent ch'ged. x.	$A-x$.	$B-x$.	K.	K (cor.).
30	4.82	67.0	18.82	25.6	1370	74.4	0.0177	0.0183
60	8.15	64.9	18.23	44.7	1350	55.3	0.0179	0.0185
90	9.12	55.8	15.68	58.2	1337	41.8	0.0177	0.0183
120	10.95	56.5	15.88	69.9	1325	30.1	0.0184	0.0190
150	12.80	59.3	16.65	76.8	1318	23.2	0.0180	0.0186
180	15.07	62.8	17.64	85.4	1310	14.6	0.0198	0.0205
210	23.15	95.4	26.80	86.4	1309	13.6	0.0176	0.0182

m-Hydroxybenzamide, 2.773 Grams in 500 cc.

30	3.75	63.9	17.95	20.9	1374	79.1	0.0140	0.0145
60	5.51	55.6	15.62	34.6	1360	65.4	0.0128	0.0132
90	7.96	66.5	18.69	42.6	1352	57.4	0.0112	0.0116
120	8.09	57.7	16.21	49.9	1345	50.1	0.0105	0.0109
150	10.55	67.7	19.02	58.1	1337	41.9	0.0106	0.0110
180	9.77	57.8	16.24	60.0	1335	40.0	0.0093	0.0096
210	16.62	94.0	26.41	63.0	1332	37.0	0.0087	0.0090

SERIES IV.

HCl $= A = 0.5603$, $B = 0.2013$, $A-B = 0.5402$, $A/B = 27.83$. Temp. 99°.82 C.

m-Iodobenzamide, 1.981 Grams in 400 cc.

30	2.01	58.7	8.24	24.4	2759	75.6	0.0167	0.0175
60	4.24	66.8	9.38	45.2	2738	54.8	0.0181	0.0190
90	5.53	67.4	9.47	58.4	2725	41.6	0.0176	0.0185
120	7.12	70.0	9.83	72.4	2711	27.6	0.0195	0.0204
150	6.10	52.2	7.83	77.8	2705	22.2	0.0182	0.0191
180	9.03	73.0	10.25	88.1	2695	11.9	0.0216	0.0227

p-Iodobenzamide, 1.981 Grams in 400 cc.

30	1.70	56.4	7.92	21.5	2762	78.5	0.0146	0.0153
60	4.09	69.3	9.73	42.0	2741	58.0	0.0163	0.0171
90	4.81	62.8	8.82	54.5	2729	45.5	0.0158	0.0166
120	4.95	67.0	9.41	63.2	2720	36.8	0.0151	0.0158
150	5.64	55.2	7.75	72.8	2710	27.2	0.0158	0.0166
180	6.81	62.1	8.72	78.1	2705	21.9	0.0153	0.0160

SERIES V.*

HCl = A = 0.5408, B = 0.04026, $A-B$ = 0.5005, A/B = 13.43. Temp. 99°.78 C.

o-Brombenzamide, 4.816 Grams.

t.	Charged.	Volume of sample.	Equivalent of sample.	Per cent charged, x.	$A-x$.	$B-x$.	K.	K (cor.).
60	1.12	64.7	17.73	6.3	1337	93.7	0.00101	(0.00212)
165	3.11	80.9	22.17	14.0	1329	86.0	0.00170	0.00178
210	3.45	72.9	19.96	17.3	1326	82.7	0.00168	0.00177
240	3.59	67.5	18.50	19.4	1324	80.6	0.00167	0.00176
270	4.08	69.0	18.91	21.6	1321	78.4	0.00168	0.00176
300	3.91	59.2	16.22	24.1	1319	75.9	0.00172	0.00180
330	5.11	72.2	19.78	25.8	1317	74.2	0.00169	0.00178

RECAPITULATION.

Constants of Amides with Hydrochloric Acid—Constant of Benzamide, 0.0217.

o-Phenoxy-	*o*-Phenoxy- ½ Conc.	*o*-Dimethylamido-	*o*-Brom-	*p*-Methoxy-
(0.00799)	0.00562	0.00103	(0.00212)	0.0125
0.00688	0.00572	0.00130	0.00178	0.0132
0.00557	0.00532	0.00103	0.00177	0.0127
0.00597	0.00570	0.00118	0.00176	0.0128
0.00518	0.00568	0.00123	0.00176	0.0129
0.00537	0.00549	0.00123	0.00180	0.0137
0.00503	0.00595	0.00121	0.00178	0.0139
0.00536	0.00593	0.00118	.....	.....
0.00562	0.00568	0.00120	0.00177	0.0131

p-Ethoxy-	*m*-Hydroxy-	*m*-Iodo- ½ Conc.	*p*-Iodo- ½ Conc.
0.0183	0.0145	0.0175	0.0153
0.0185	0.0132	0.0190	0.0171
0.0183	0.0116	0.0185	0.0166
0.0190	0.0109	0.0204	0.0158
0.0186	0.0110	0.0191	0.0166
(0.0205)	0.0096	(0.0227)	0.0160
0.0182	0.0090	.....	.....
0.0185	0.0114	0.0189	0.0164

Summary of Average Velocities with Hydrochloric Acid.

All results are multiplied by 10,000 so as to obtain whole numbers, and those quoted from the former article are further increased 4 per cent so as to compare directly with those given above.

Benzamide, 217.

o-Cl	33.3	*o*-Br	17.7	*o*-I	11.0	....	
o-OH	45.4	*o*-OCH_3	121.0	*o*-OC_2H_5	97.0	*o*-OC_6H_5	56
o-NO_2	5.6	(*o*-NH_2	17.8)	(*o*-$N(CH_3)_2$	12.0	....	
o-CH_3	22.7	....		....		....	
....		*m*-Br	218	*m*-I	189		
p-Cl	208	*p*-Br	204	*p*-I	164		
m-NO_2	204	*m*-NH_2	185	*m*-CH_3	201		
p-NO_2	245	*p*-NH_2	198	*p*-CH_3	183		
p-OCH_3	131	*p*-OC_2H_5	185				

Discussion of Results.

The results obtained in this work are in line with those already published. Amides having groups in the meta and para positions are hydrolyzed more slowly than benzamide. Paranitrobenzamide is the only exception to this rule that I have found so far. The retardation is not great, though *p*-methoxybenzamide is surprisingly stable. The results with the halogens are not strictly comparable with the others as, on account of their slight solubility, only half the regular concentration could be used with them. This makes them go something like 10 per cent faster than they would have done at the usual concentration. Among the halogens, iodine retards more than bromine, and bromine more than chlorine, while the halogen has more effect in the para position than in the meta. With all the groups the nature is of more importance than the mere weight, as NH_2 retards more than NO_2 or bromine, and almost as much as iodine, when all are in the para position.

Three additional ortho amides are presented in this article, *o*-phenoxy, *o*-dimethylamido, and *o*-brombenzamide. They simply strengthen the conclusions reached in the former paper, namely, that ortho groups greatly retard the hydrolysis of

benzamide. As seen in the table above, the halogens stand in their proper order. An iodine atom, in the ortho position, retards the hydrolysis 94.9 per cent, a bromine atom 91.9 per cent, and a chlorine atom only 84.6 per cent. The phenoxy group shows itself nearly analogous to the methoxy and ethoxy groups, though all three of them retard far less than hydroxyl. Kellas, in his work on esterification, wrote out the series,

$$—OH, \qquad —OCH_3, \qquad OC_2H_5,$$

and supposed that they would give analogous results. The values here given show, once more, that —OH is no more analogous to $—OCH_3$ than than the H— of formic acid is to the CH_3— of acetic. As for the rest, no further remarks are needed except to say that I regret that I have doubts as to the orthoamidobenzamide used in former experiments.

Hydrolysis of Amides with Barium Hydrate.

The experiments here given divide themselves, chronologically, into two groups, those included in Series I. to VI., and those that follow, the two being separated by a considerable interval of time. In the last the same preparations of the amides were used as in the first, but different and more carefully calibrated burettes and other apparatus as well as new standard solutions. The method of working was the same as that previously used for orthonitrobenzamide, that is, an Erlenmeyer flask holding about 125 cc., was fitted with a rubber stopper carrying a glass tube about 30 cm. long, bent over at the top and fitting into the stopper of a U-tube. The desired amount of amide was weighed into the dried flask and 75 cc. of the baryta water measured in, the U-tube attached, and more than enough hydrochloric acid put in the U-tube to neutralize the alkali in the flask. The flask was plunged into boiling water and shaken so as to effect the solution of the amide as quickly as possible. At the end of the desired time the flask was taken out and plunged into cold water. By tilting it at the right moment the acid in the U-tube can be made to suck back into the flask in order to stop the reaction and fix the ammonia. The whole contents of the flask was washed into the still, and the ammonia estimated in the usual way. In a series of experiments, by this method, there are

many difficulties in the way of obtaining concordant results. A number of such flasks were always prepared at the same time, and four of them were usually heated in the same bath. As some of the amides, especially the amido, are very soluble in water while others, such as the parabrom- and iodo- and orthophenoxybenzamide are nearly insoluble, requiring several hundred parts of boiling water for their solution, the timing of the reaction is not accurate. Half a minute was allowed on each timing to allow for heating and solution. Sometimes the same amide, in two flasks treated exactly alike, would dissolve more quickly in one than in the other. As the ammonia liberated in the reaction is not held by the hot alkali, there is considerable danger of its escaping if the stopper is not perfectly tight. There is one advantage, and that is that the experiments are perfectly independent, as each flask is treated individually, and when they do support each other there is more assurance that the results are correct. The agreement of the results of a series is not what was desired, and sometimes the averages of two series do not agree as they might, but in nearly all cases the velocity is determined exactly enough to define clearly the relations of the various amides. The baryta water used was made up, 2 liters at a time, from a strong stock solution, and the strength of each lot determined by titration. 75 cc. of this were measured into each flask from an automatic pipette connected with the bottle and protected from the carbon dioxide of the air. In Series I the possibility of readily and completely decomposing, by means of strong alkali, the amides used, made it easier to employ the method previously used for *m*- and *p*-nitrobenzamides, that is, the amide was weighed into a large flask with 600 cc. baryta water and measured samples taken out. The free ammonia was distilled off with magnesium hydroxide and thrown away, and the residual amide estimated by distilling with strong caustic soda.

As for the remaining experiments, the effort was made to make them as nearly uniform as possible. The amide was, as before, weighed into the carefully cleaned and dried Erlenmeyer flasks. A large bottle full of rather strong baryta water was prepared and, by means of an automatic pipette, 17.56 cc. of this added to

each flask into which had just been put the water from two other automatic pipettes holding 6.87 and 50.57 cc., respectively, the three making just 75 cc. The water used had been distilled from acid chromate and alkaline permanganate solutions. The water and baryta solutions were well protected with soda-lime tubes both while in the pipettes and while in the containers. The baryta water, so diluted, was always perfectly clear in the flasks and showed no trace of carbonate. Many experiments were lost on account of the breaking of the flasks, the most fatal time being the moment when they were plunged into cold water to stop the reaction. Continued heating with baryta water etches the glass and renders it very brittle. The strength of the diluted baryta water was determined by titration. For this, and for the estimation of the ammonia, hydrochloric acid 14.66 N was used. To standardize this 0.500 gram *p*-nitrobenzamide was weighed into each of four distilling flasks, water and 5 grams of caustic soda added and distilled, the ammonia being caught in a measured portion of the acid to be standardized. One stopper was found to be defective and that flask rejected. The ammonia from the other three neutralized 20.55, 20.54, and 20.55 cc., respectively, of the acid. 20.55 cc. of the acid was taken to be equivalent to 0.500 gram *o*-nitrobenzamide and as, with few exceptions, the amount of amide used in any experiment was equivalent to that, this figure was used directly in calculating the per cent of decomposition. I would like to recommend this method of standardizing acid, to chemists in general, and especially to those engaged on ammonia work, who have the stills already set up. To one so prepared, it is the quickest and simplest that I know of, and gives results under the actual working conditions with the same amounts of materials, indicators and the like as are employed in the usual determinations. Paranitrobenzamide is particularly well adapted for such service. It need not be weighed with extreme care since owing to its rather high molecular weight, it yields, on hydrolysis, only a little over 10 per cent of its weight of ammonia. Paranitrobenzoic acid is a commercial article or may be easily and cheaply prepared by the pound, from commercial paranitrotoluene. It is purified by one crystallization or

even by solution in soda and precipitation of the filtered solution by acid. It is readily converted into the amide. The amide crystallizes well from hot water, in which it is only slightly soluble, and may be obtained perfectly pure at one crystallization. It forms, when the water solution is rapidly cooled, dense fine grains easy to weigh and contains no water of crystallization. It is easily identified by its melting-point, and as it melts at 201°.4 C., it may safely be dried in an air-bath. It yields the calculated amount of ammonia when distilled in the usual way with alkali, just as readily and as surely as an equivalent amount of any ammonium salt. It may be kept for years without alteration.

SERIES I.

$Ba(OH)_2 = A = 0.0984$, $B = 0.04026$, $A - B = 0.0581$, $A/B = 2.445$. Temp. 100° C.

m-Amidobenzamide, 3.712 Grams.

t.	Unchanged.	Volume of sample.	Equivalent of sample.	Per cent changed, x.	$A-x$.	$B-x$.	K.	K (cor.).
30	15.64	70.5	19.81	21.1	223.4	78.9	0.0836	0.0869
60	12.12	70.5	19.81	38.8	205.7	61.2	0.0907	0.0943
90	10.57	73.7	20.71	49.0	195.5	51.0	0.0854	0.0888
120	8.61	73.6	20.68	58.4	186.1	41.6	0.0860	0.0894
150	7.04	73.2	20.56	65.8	178.7	34.2	0.0866	0.0900
180	6.04	74.9	21.02	71.3	173.2	28.7	0.0858	0.0892
210	5.26	74.6	20.96	74.9	169.6	25.1	0.0827	0.0860
240	4.97	80.1	22.50	77.9	166.6	22.1	0.0802	0.0834

m-Toluicamide, 3.256 Grams.

30	15.58	71.9	20.20	22.9	221.6	77.1	0.0921	0.0958
60	12.35	72.1	20.25	39.0	205.5	61.0	0.0913	0.0945
90	10.50	69.3	19.47	46.1	198.4	53.9	0.0777	0.0808
120	8.57	67.5	18.96	54.8	189.7	45.2	0.0770	0.0801
150	7.60	71.5	20.08	62.2	182.3	37.8	0.0774	0.0805
180	6.47	69.1	19.41	66.7	177.8	33.3	0.0742	0.0772
210	6.08	74.1	20.82	70.3	174.2	29.7	0.0712	0.0740
240	6.08	86.3	24.21	74.9	169.6	25.1	0.0724	0.0753

p-Toluicamide, 3.256 Grams.

30	15.12	63.8	17.92	15.6	228.9	84.4	0.0591	0.0615
60	13.01	69.3	19.47	33.2	211.3	66.8	0.0734	0.0763
90	11.94	71.5	20.08	40.5	204.0	59.5	0.0642	0.0668
120	11.86	71.4	20.06	41.9	202.6	58.1	0.0506	0.0526
150	9.09	74.7	21.00	56.7	187.8	43.3	0.0653	0.0679
180	8.63	77.5	21.77	60.4	184.1	39.6	0.0610	0.0634
210	7.20	73.5	20.65	65.1	179.4	34.9	0.0605	0.0629
240	6.20	66.3	18.63	66.8	177.7	33.2	0.0588	0.0612

In Series II, and in those that follow, the volume of the sample is always 75 cc. as the whole contents of the small flask is used and the equivalent of the sample 20.55 for the usual concentration or 10.27 for half concentration. For this reason the two columns containing these values are omitted. The second column gives the number of cubic centimeters of standard acid that the ammonia from the hydrolyzed amide neutralized. The other columns are the same as in the series above. In the first six series the temperature, when known exactly, is put at the beginning of the series. In those that follow, the temperature is put in the second column of figures, aud to save figures it is given as the amount, in degrees, above 100° C., using the minus sign when below. This temperature correction was found from the barometer reading.

Series II.

$Ba(OH)_2 = A = 0.1012$, $B = 0.04026$, $A - B = 0.0609$, $A/B = 2.514$. Temp. 89°.89 C.

o-Toluicamide, 0.407 Gram.

t.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (cor.).
30	0.42	2.0	249.4	98.0	0.00669	0.00699
60	0.66	3.1	248.3	96.9	0.00522	0.00546
90	0.85	4.0	247.4	96.0	0.00454	0.00475
120	1.00	4.8	246.6	95.2	0.00408	0.00426
150	1.79	7.1	244.3	92.9	0.00492	0.00514
180	1.88	8.9	242.5	91.1	0.00522	0.00546
210	1.98	9.4	242.0	90.6	0.00473	0.00494
240	2.29	10.8	240.6	89.2	0.00480	0.00502

o-Chlorbenzamide, 4.688 Grams. Temp. 100°.02 C.

30	2.61	12.4	239.0	87.6	0.0447	0.0464
60	4.67	22.1	229.3	77.9	0.0431	0.0448
120	7.62	36.1	215.3	63.9	0.0401	0.0417
150	9.13	43.3	208.1	56.7	0.0439	0.0456
180	10.75	50.9	200.5	49.1	0.0380	0.0395
240	12.25	58.0	133.4	42.0	0.0414	0.0430

SERIES III.

$Ba(OH)_2 = A = 0.1030$, $B = 0.04026$, $A-B = 0.0627$, $A/B = 2.559$.

o-Hydroxybenzamide, 0.416 Gram. Temp. 100°.02 C.

t.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (cor.).
30	0.66	3.1	252.8	96.9	0.01149	0.01193
60	0.93	4.4	251.5	95.6	0.00723	0.00751
90	1.26	6.0	249.9	94.0	0.00646	0.00671
120	1.42	6.8	249.1	93.2	0.00576	0.00598
150	1.68	8.0	247.9	92.0	0.00547	0.00568
180	2.04	9.7	246.2	90.3	0.00562	0.00584
240	2.42	11.5	244.4	88.5	0.00507	0.00527

Benzamide, 0.365 Gram. Temp. 99°.92 C.

30	4.93	23.4	233.2	76.6	0.0905	0.0945
60	8.48	40.2	216.4	59.8	0.0909	0.0949
90	10.07	52.5	204.1	47.5	0.0909	0.0949
120	12.96	61.4	195.2	38.6	0.0897	0.0936
150	14.28	67.7	188.9	32.3	0.0872	0.0910
180	15.06	71.4	185.2	28.6	0.0816	0.0852

SERIES IV.

$Ba(OH)_2 = A = 0.1097$, $B = 0.04026$, $A-B = 0.0694$, $A/B = 2.725$.

o-Nitrobenzamide, 0.500 Gram. Temp. 99°.84 C.

30	3.03	14.2	259.3	85.8	0.0491	0.0522
60	4.82	22.6	249.9	77.4	0.0407	0.0427
90	6.41	30.1	242.4	69.9	0.0386	0.0405
120	7.33	34.4	238.1	65.6	0.0345	0.0362
150	7.90	37.1	235.4	62.9	0.0305	0.0320
180	8.58	40.3	232.2	59.7	0.0285	0.0299
210	9.15	43.0	229.5	57.0	0.0268	0.0281
240	9.80	46.0	226.5	54.0	0.0256	0.0272

m-Nitrobenzamide, 0.500 Gram. Temp. 100° C.

30	17.23	81.0	191.0	19.0	0.627	0.652
60	19.65	92.4	180.1	7.6	0.519	0.540
90	20.63	97.0	175.5	3.0	0.491	0.511

SERIES V.

$Ba(OH)_2 = A = 0.1033$, $B = 0.04026$, $A - B = 0.0630$, $A/B = 2.566$.

p-Amidobenzamide, 0.410 Gram. Temp. 100° C.

t.	Changed.	Per cent changed, *x*.	*A*−*x*.	*B*−*x*.	*K*.	*K* (cor.).
30	1.40	6.6	250.0	93.4	0.0223	0.0232
60	2.38	11.2	245.4	88.8	0.0196	0.0204
90	3.53	16.6	240.0	83.4	0.0202	0.0210
120	4.47	21.0	235.6	79.0	0.0199	0.0207
180	6.19	29.1	227.5	70.9	0.0197	0.0205
210	6.76	31.7	224.9	68.3	0.0189	0.0197
240	7.36	34.5	222.1	65.5	0.0184	0.0192

SERIES VI.

$Ba(OH)_2 = A = 0.1030$, $B = 0.04026$, $A - B = 0.0627$, $A/B = 2.559$.

o-Iodobenzamide, 0.743 Gram. Temp. 99°.75 C.

30	1.06	5.0	250.9	95.0	0.0168	0.0177
60	1.79	8.4	247.5	91.6	0.0144	0.0151
90	2.31	10.8	245.1	89.2	0.0126	0.0133
150	3.59	16.8	239.1	83.2	0.0123	0.0129
180	4.05	19.0	236.9	81.0	0.0118	0.0124
210	4.49	21.1	234.8	78.9	0.0115	0.0121
240	5.08	23.9	232.0	76.1	0.0116	0.0122

o-Methoxybenzamide, 0.455 Gram. Temp. 100° C.

60	5.51	25.9	230.0	74.1	0.0514	0.0534
120	9.11	42.9	213.0	57.1	0.0501	0.0521
150	10.19	47.0	208.9	53.0	0.0460	0.0478
180	11.72	55.1	200.8	44.9	0.0495	0.0515
210	13.16	61.9	194.0	38.1	0.0523	0.0544
240	13.88	65.3	190.6	34.7	0.0508	0.0528

p-Methoxybenzamide, 0.455 Gram. Temp. 99°.67 C.

60	5.09	23.6	232.3	76.4	0.0455	0.0480
90	7.03	33.0	222.9	67.0	0.0465	0.0491
120	8.55	40.1	215.8	59.9	0.0442	0.0467
180	10.50	49.4	206.5	50.6	0.0417	0.0440
210	11.68	54.9	201.0	45.1	0.0421	0.0445
240	12.76	60.1	195.8	39.9	0.0426	0.0450

SERIES VI (*Continued*).

o-Ethoxybenzamide, 0.497 Gram. Temp. 100° C.

t.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (cor.)
120	7.00	32.9	223.0	67.1	0.0347	0.0361
180	9.42	44.2	211.7	55.8	0.0349	0.0363
240	11.14	52.4	203.5	47.6	0.0341	0.0355

o-Dimethylamidobenzamide, 0.494 Gram. Temp. 100° C.

60	1.88	8.8	247.1	91.2	0.0152	0.0158
120	3.49	16.4	239.5	83.6	0.0150	0.0156
150	4.12	19.3	236.6	80.7	0.0145	0.0151
180	4.65	21.8	234.1	78.2	0.0139	0.0145
210	5.48	25.7	230.2	74.3	0.0145	0.0151
240	6.02	28.3	227.6	71.7	0.0144	0.0150

m-Hydroxybenzamide, 0.416 Gram. Temp. 100° C.

60	1.56	7.4	248.5	92.6	0.0126	0.0131
90	2.53	12.0	243.9	88.0	0.0141	0.0147
150	5.02	23.8	232.1	76.2	0.0185	0.0192
180	6.00	28.4	227.5	71.6	0.0191	0.0199
210	6.47	30.6	225.3	69.4	0.0181	0.0189
240	7.08	33.5	222.9	66.5	0.0159	0.0165

Series VII.

Benzamide, 0.365 Gram.

$Ba(OH)_2 = A = 0.10416$, $B = 0.04026$, $A-B = 0.0639$, $A/B = 2.592$.

t.	Temperature correction.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (cor.).
30	—0.01	4.14	20.1	239.1	79.9	0.0751	0.0781
60	"	8.55	41.6	217.6	58.4	0.0944	0.0982
90	"	11.07	53.9	205.3	46.1	0.0941	0.0979
120	"	13.18	64.1	195.1	35.9	0.0965	0.1004
150	"	14.73	71.7	187.5	28.3	0.0979	0.1018
210	"	16.57	80.6	178.6	19.4	0.0944	0.0982
270	—0.34	17.61	85.7	173.5	14.3	0.0895	0.0945
300	"	18.00	87.6	171.6	12.4	0.0874	0.0954
330	"	18.35	89.5	169.7	10.5	0.0868	0.0917
360	"	19.14	93.1	166.1	6.9	0.0969	0.1023
30	"	4.48	21.8	237.4	78.2	0.0824	0.0871
60	"	7.89	38.4	220.8	61.6	0.0845	0.0893
90	"	10.69	52.0	207.2	48.0	0.0887	0.0937
120	"	12.72	61.9	197.3	38.1	0.0903	0.0954
150	"	14.10	68.6	190.6	31.4	0.0888	0.0938
180	"	15.27	74.3	184.9	25.7	0.0887	0.0938
210	"	16.26	79.1	180.1	20.9	0.0895	0.0946
240	"	16.95	82.5	176.7	17.5	0.0887	0.0937

p-Amidobenzamide, 0.410 Gram.

30	..	1.20	5.8	253.4	94.2	0.0194	0.0202
60	..	2.05	10.0	249.2	90.0	0.0172	0.0179
90	..	3.05	14.8	244.3	85.1	0.0170	0.0176
120	..	3.80	18.5	240.7	81.5	0.0170	0.0177
150	..	4.58	22.3	236.9	77.7	0.0169	0.0176
180	..	5.42	26.4	232.8	73.6	0.0173	0.0180
210	..	6.05	29.4	229.8	70.6	0.0168	0.0174
240	..	6.11	29.7	229.5	70.3	0.0150	0.0156
300	—0.08	8.41	40.9	218.3	59.1	0.0185	0.0193
360	0.00	9.27	45.1	214.1	54.9	0.0178	0.0185
420	—0.08	10.21	49.7	209.5	50.3	0.0177	0.0185
450	0.00	10.43	50.7	208.5	49.3	0.0170	0.0177
480	0.00	10.65	51.8	207.4	48.2	0.0165	0.0172
540	..	11.87	57.8	204.1	42.2	0.0177	0.0184
840	..	14.38	70.0	189.2	30.0	0.0166	0.0172

SERIES VII (*Continued*).

m-Amidobenzamide, 0.464 Gram.

t.	Temperature correction.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	K (cor.).
31½	0.11	4.79	23.3	235.9	76.7	0.0893	0.0922
60	"	7.92	36.4	222.8	63.6	0.0786	0.0811
90	"	10.33	50.3	208.9	49.7	0.0840	0.0867
150	"	13.82	67.3	191.9	32.7	0.0853	0.0880
180	"	15.14	73.7	185.5	26.3	0.0870	0.0899
210	"	16.05	78.1	181.1	21.9	0.0864	0.0893
240	"	16.70	81.3	177.9	18.7	0.0848	0.0876

o-Chlorbenzamide, 0.468 Gram.

30	0.07	2.82	13.7	245.5	86.3	0.0485	0.0503
60	"	5.21	25.4	233.8	74.6	0.0495	0.0501
150	"	9.94	48.4	210.8	51.6	0.0475	0.0492
180	"	10.91	53.1	206.1	46.9	0.0459	0.0475
210	"	11.67	56.8	202.4	43.2	0.0441	0.0457
240	"	12.89	62.7	196.5	37.3	0.0462	0.0479
270	"	14.04	68.3	190.9	31.7	0.0489	0.0506
300	"	14.47	70.4	188.8	29.6	0.0470	0.0486
330	"	15.25	74.2	185.0	25.8	0.0482	0.0500
360	"	15.65	76.2	183.0	23.8	0.0473	0.0490

o-Hydroxybenzamide, 0.416 Gram.

30	—0.12	0.54	2.6	256.6	97.4	0.0085	0.0088
60	"	0.84	4.1	255.1	95.9	0.0068	0.0070
90	"	1.20	5.8	253.4	94.2	0.0064	0.0067
120	"	1.46	7.1	252.1	92.9	0.0060	0.0062
150	"	1.62	7.9	251.3	92.1	0.0054	0.0056
180	"	1.84	9.0	250.2	91.0	0.0051	0.0053
210	"	2.23	10.9	248.3	89.1	0.0054	0.0056
240	"	2.50	12.2	247.0	87.8	0.0053	0.0055
330	"	3.06	14.9	244.3	85.1	0.0048	0.0050
360	"	3.35	16.3	242.9	83.7	0.0049	0.0051
390	"	3.44	16.7	242.5	83.3	0.0046	0.0048
420	"	3.55	17.3	241.9	82.7	0.0045	0.0047

o-Brombenzamide, 0.602 Gram.

60	—0.09	3.31	16.1	243.1	83.9	0.0290	0.0302
120	"	5.85	28.5	230.7	71.5	0.0286	0.0297
180	"	7.62	37.1	222.1	62.9	0.0269	0.0280
240	"	9.30	45.3	213.9	54.3	0.0273	0.0284

SERIES VII (*Continued*).

m-Toluicamide, 0.407 Gram.

t.	Temperature correction.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (Cor.).
30	—0.19	3.73	18.2	241.0	81.8	0.0668	0.0701
60	"	7.03	34.2	225.0	65.8	0.0722	0.0756
90	—0.34	9.19	44.7	214.5	55.3	0.0701	0.0712
120	"	10.64	51.8	207.4	48.2	0.0661	0.0697
150	—0.19	13.42	65.3	193.9	34.7	0.0801	0.0846
180	"	14.36	69.9	189.3	30.1	0.0771	0.0814
210	"	15.04	73.2	186.0	26.8	0.0734	0.0745
240	"	15.84	77.1	182.1	22.9	0.0731	0.0742

m-Brombenzamide, 0.602 Gram.

30	0.08	10.52	51.2	208.0	48.8	0.259	0.272
60	"	15.13	73.6	185.6	26.4	0.260	0.273
90	"	17.54	85.4	173.8	14.6	0.265	0.278
120	"	18.73	91.1	168.1	8.9	0.259	0.271

SERIES VIII.

$Ba(OH)_2 = A = 0.10416$, $B = 0.03746$, $A-B = 0.0667$, $A/B = 2.800$.

p-Toluicamide, 0.379 Gram.

30½	0.16	3.12	16.3	263.7	83.7	0.0589	0.0607
60	"	5.47	28.6	251.4	71.4	0.0572	0.0591
90	"	7.36	38.5	241.5	61.5	0.0563	0.0582
120	"	9.07	47.4	232.6	52.6	0.0571	0.0590
180	"	11.73	61.4	218.6	38.6	0.0586	0.0606
210	"	12.61	65.9	214.1	34.1	0.0576	0.0596
240	"	13.44	70.3	209.7	29.7	0.0578	0.0597

o-Toluicamide, 9.379 Gram.

30	0.13	0.31	1.6	278.4	98.4	0.0052	0.0053
60	"	0.59	3.1	276.9	96.9	0.0051	0.0053
90	"	0.90	4.7	275.3	95.3	0.0052	0.0054
120	"	1.06	5.5	274.5	94.5	0.0046	0.0048
150	"	1.39	7.3	272.7	92.7	0.0049	0.0051
180	"	1.54	8.6	271.4	91.4	0.0049	0.0051
210	"	1.91	10.0	270.0	90.0	0.0049	0.0051
240	"	1.99	10.4	269.6	89.6	0.0046	0.0047
630	"	2.68	14.0	266.0	86.0	0.0045	0.0047
660	"	2.94	15.4	264.6	84.6	0.0046	0.0048

Series IX.

$Ba(OH)_2 = A = 0.10416$, $B = 0.02013$, $A-B = 0.08403$, $A/B = 5.184$.

m-Brombenzamide, 0.301 Gram.

t.	Temperature correction.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (Cor.).
30	—0.07	5.61	54.6	463.8	45.4	0.275	0.287
60	"	7.92	77.1	441.3	22.9	0.267	0.278
90	"	9.04	88.0	430.4	12.0	0.262	0.273
120	"	9.57	93.1	425.3	6.9	0.251	0.262
150	"	10.03	97.6	420.8	2.4	0.286	0.298
180	"	10.14	98.7	419.7	1.3	0.280	0.292

m-Iodobenzamide, 0.371 Gram.

30	0.13	5.90	57.4	461.0	42.6	0.299	0.310
60	"	7.58	73.5	444.9	26.5	0.239	0.248
90	"	8.72	84.9	433.5	15.1	0.232	0.240
120	"	9.52	92.7	425.7	7.3	0.246	0.254
150	"	9.77	95.1	423.3	4.9	0.228	0.237

p-Chlorbenzamide, 0.234 Gram.

30	—0.13	4.86	47.3	471.1	52.7	0.221	0.231
60	"	6.92	67.3	451.1	32.7	0.199	0.208
90	"	7.61	74.1	444.3	25.7	0.162	0.169
120	"	8.72	84.9	433.5	15.1	0.174	0.182
150	"	9.22	89.7	428.7	10.3	0.169	0.177
180	"	9.73	94.7	423.7	5.3	0.185	0.193
210	"	9.82	95.6	422.8	4.4	0.169	0.177
240	"	9.97	97.0	421.4	3.0	0.167	0.175
30	0.00	4.11	40.0	478.4	60.0	0.175	0.182
60	"	6.40	63.3	455.1	36.7	0.177	0.184
90	"	7.64	74.4	444.0	25.6	0.163	0.170
120	"	8.69	84.6	433.8	15.4	0.172	0.179
180	"	9.57	93.1	425.3	6.9	0.168	0.175
210	"	9.75	94.9	423.5	5.1	0.161	0.167

SERIES IX (*Continued*).

p-Brombenzamide, 0.301 Gram.

t.	Temperature correction.	Changed.	Per cent changed, *x*.	*A*—*x*.	*B*—*x*.	*K*.	*K* (Cor.).
30	—0.08	4.14	40.3	478.1	59.7	0.177	0.185
60	"	6.64	64.6	453.8	35.4	0.184	0.192
90	"	8.22	80.0	438.4	20.0	0.195	0.204
120	"	8.86	86.2	432.2	13.8	0.183	0.191
150	"	9.33	90.8	427.6	9.2	0.178	0.186
180	"	9.58	93.2	425.2	6.8	0.168	0.176
30	0.00	4.04	39.3	479.1	60.7	0.171	0.177
60	"	6.36	61.9	456.5	38.1	0.170	0.177
90	"	7.79	75.8	442.6	24.2	0.171	0.177
180	"	9.45	92.0	426.4	8.0	0.158	0.164
210	"	9.61	93.5	424.9	6.5	0.147	0.153

p-Iodobenzamide, 0.371 Gram.

30	—0.13	3.59	34.9	483.5	65.1	0.146	0.153
60	"	5.89	57.3	461.1	42.7	0.149	0.156
90	"	7.52	73.2	445.2	26.8	0.158	0.165
120	"	8.44	82.1	436.3	17.9	0.157	0.164

o-Phenoxybenzamide, 0.321 Gram.

30	—0.01	1.25	12.2	506.2	87.8	0.0422	0.0439
60	"	2.32	22.6	495.8	77.4	0.0420	0.0437
90	"	3.16	30.8	487.6	69.2	0.0406	0.0422
180	"	5.05	49.1	469.3	50.9	0.0350	0.0364
210	"	5.81	56.5	461.9	43.5	0.0406	0.0423
240	"	6.11	59.5	458.9	40.5	0.0386	0.0402
270	"	6.72	65.4	453.0	34.6	0.0408	0.0425
360	"	7.81	76.0	442.4	24.0	0.0419	0.0436
420	"	8.40	81.7	436.7	18.3	0.0433	0.0450
450	"	8.31	80.9	437.5	19.1	0.0394	0.0410

Series X.

o-Nitrobenzamide, 0.500 Gram.

$Ba(OH)_2 = A = 0.10416$, $B = 0.04026$, $A - \frac{1}{2}B = 0.08403$, $A/\frac{1}{2}B = 5.184$. Temp. 100° C.

t.	Changed.	Per cent changed, *x.*	*A*—2*x.*	*B*—2*x.*	*K* (Cor.).
30	2.67	13.0	492.4	74.0	0.1054
60	4.52	22.0	474.4	56.0	0.1036
90	5.90	28.7	461.0	42.6	0.1021
120	6.65	32.4	453.6	35.2	0.0961
150	7.53	36.6	445.2	26.8	0.0983
180	8.02	39.0	440.4	22.0	0.0951
210	8.49	41.3	435.8	17.4	0.0947
240	8.87	43.2	432.0	13.6	0.0956
300	9.34	45.6	427.2	8.8	0.0944
360	9.99	48.6	421.2	2.8	(0.1185)
420	9.93	48.3	421.8	3.4	0.0957
480	10.31	50.1	....	....	....
900	10.21	49.7	....	....	....
1500	10.03	48.8	....	....	....

Recapitulation.

Constants of Amides with Barium Hydrate.—Constant of Benzamide, 0.0943.

o-Toluic.	*o*-Nitro-	*o*-Chlor-	*o*-Hydroxy-	*o*-Brom-	*o*-Iodo-
(0.00699)	0.0522	0.0464	(0.01193)	0.0302	0.0177
0.00546	0.0427	0.0448	0.00751	0.0297	0.0151
0.00475	0.0405	0.0417	0.00671	0.0280	0.0133
0.00426	0.0362	0.0456	0.00598	0.0284	0.0129
0.00514	0.0320	0.0395	0.00568	....	0.0124
0.00546	0.0299	0.0430	0.00584	....	0.0121
0.00494	0.0281	....	0.00527	....	0.0122
0.00502	0.0272	....	....	....	....
0.00508		0.0435	0.00616	0.0291	0.0130

RECAPITULATION (*Continued*).

o-Hydroxy-	*o*-Methoxy-	*o*-Ethoxy-	*o*-Dimethylamido-	*o*-Phenoxy- ½ Conc.	*o*-Toluic.
0.0088	0.0534	0.0361	0.0158	0.0439	0.0053
0.0070	0.0521	0.0363	0.0156	0.0437	0.0053
0.0067	0.0478	0.0355	0.0151	0.0422	0.0054
0.0062	0.0515	....	0.0145	0.0364	0.0048
0.0056	0.0544	....	0.0151	0.0423	0.0051
0.0053	0.0528	....	0.0150	0.0402	0.0051
0.0056	....	....	....	0.0425	0.0051
0.0055	....	....	....	0.0436	0.0047
0.0050	....	....	....	0.0450	0.0047
0.0051	....	....	....	0.0410	0.0048
0.0048	....	....	....	....	....
0.0047	....	....	....	....	....
0.0059?	0.0528	0.0360	0.0152	0.0427	0.00503

RECAPITULATION (*Continued*).

o-Chlor-	Benzamide.	Benzamide.	*m*-Amido-	*m*-Amido-	*p*-Amido-
0.0503	0.0945	0.0945	0.0922	0.0869	(0.0202)
0.0501	0.0949	0.0954	0.0811	0.0943	0.0179
0.0492	0.0949	0.0917	0.0861	0.0888	0.0176
0.0475	0.0936	0.1023	0.0880	0.0894	0.0177
0.0457	0.0910	0.0871	0.0899	0.0900	0.0176
0.0479	0.0852	0.0893	0.0893	0.0892	0.0180
0.0506	0.0781	0.0937	0.0876	0.0860	0.0174
0.0486	0.0982	0.0954	....	0.0834	0.0156
0.0500	0.0979	0.0938	....	....	0.0193
0.0490	0.1004	0.0938	....	....	0.0185
....	0.1018	0.0946	....	....	0.0185
....	0.0982	0.0937	....	....	0.0177
....	....	....	....	....	0.0172
....	....	....	....	....	0.0184
....	....	....	....	....	0.0172
0.0489	0.0943		0.0877	0.0885	0.0178

RECAPITULATION (*Continued*).

p-Chlor- ½ Conc.	*p*-Brom- ½ Conc.	*m*-Brom- ½ Conc.	*m*-Brom- Regular conc.	*p*-Iodo- ½ Conc.	*m*-Iodo- ½ Conc.	*m*-Nitro-
(0.231)	0.185	0.287	0.272	0.153	0.310	0.652
0.208	0.192	0.278	0.273	0.156	0.248	0.540
0.169	0.204	0.273	0.278	0.165	0.240	0.511
0.182	0.191	0.262	0.271	0.164	0.254	....
0.177	0.186	0.298	....	....	0.237	....
0.193	0.176	0.292	....	....	....	....
0.177	0.177	....	....	....	....	....
0.175	0.177	....	....	....	....	....
0.182	0.177	....	....	....	....	....
0.184	0.164	....	....	....	....	....
0.170	0.153	....	....	....	....	....
0.179	....	....	....	....	....	....
0.175	....	....	....	....	....	....
0.167	....	....	....	....	....	....
....	....	....	....	....	....	....
0.180	0.180	0.282	0.273	0.159	0.245	0.530

RECAPITULATION (*Continued*).

m-Toluic-	*m*-Toluic-	*p*-Toluic-	*p*-Toluic-	*p*-Amido-	*p*-Methoxy-	*m*-Hydroxy-
0.0958	0.0701	0.0615	0.0607	0.0232	0.0480	0.0131
0.0945	0.0756	0.0763	0.0591	0.0204	0.0491	0.0147
0.0808	0.0712	0.0668	0.0582	0.0210	0.0467	0.0192
0.0801	0.0697	0.0526	0.0590	0.0207	0.0440	0.0199
0.0805	0.0846	0.0679	0.0606	0.0205	0.0445	0.0189
0.0772	0.0814	0.0634	0.0596	0.0197	0.0450	0.0165
0.0740	0.0745	0.0629	0.0597	0.0192	....	....
0.0753	0.0742	0.0612	....	....	....	....
0.0780	0.0752	0.0623	0.0596	0.0202	0.0462	0.0180

Summary of Average Velocities with Barium Hydrate.

For the sake of whole numbers all of the above averages are multiplied by 10,000.

Benzamide, 944.

o-Cl	489	*o*-Br	291	*o*-I	130	....	
o-OH	60	*o*-OCH_3	528	*o*-OC_2H_5	360	*o*-OC_6H_5	427
o-CH_3	50.5	*o*-$N(CH_3)_2$	152	....		....	
....		*m*-Br	2820	*m*-I	2450	*m*-NO_2	5300
p-Cl	1800	*p*-Br	1800	*p*-I	1590	(*p*-NO_2	6300)
m-NH_2	885	*m*-CH_3	752	*m*-OH	165	....	
p-NH_2	178	*p*-CH_3	623	....		*p*-OCH_3	462

Discussion of Results.

As seen from the above tables, the decomposition velocities of the various amides show a much wider range of variation with alkali than with acid. As already remarked, there is more difficulty in getting uniform results in a series and, in several cases, a series recently made does not agree very well with one previously made. Seemingly erratic individual results have been thrown out in making up averages, and of two series, the most recent has been chosen. In nearly every series there is noticed a more or less regular falling off in the velocity as the reaction proceeds. This is to be expected from the known retarding action of salts which accumulate in the course of the reaction. The first measurement in a series often comes out much too high. In the experiments with *o*-hydroxybenzamide the velocity seems to decrease much too rapidly. This is borne out by two independent series. It may be that the reaction is of a different type and does not obey the equation assumed. Perhaps the acid hydroxyl group has something to do with this irregularity. With the concentrations used, the velocity of the reaction is rather small for convenient study but the case might repay a more thorough investigation. With alkali, as with acid, ortho substituted amides give low velocities. Among the halogens, chlorine retards much less than bromine which, in turn, retards far less than iodine. The methyl and hydroxyl groups are remarkable for their great effect. The ethoxy group retards more than the methoxy and even more than the phenoxy, though none of the three is in the same category with hydroxyl. The methoxy group, in the ortho position, retards only 44.0 per cent while hydroxyl, in the same place, retards 93.6 per cent. As concerns meta and para substituted amides, the results fall into three classes. First those in which there is a moderate retardation, the group having more influence in the para than in the meta position. This includes the toluic amides and metamidobenzamide. Second, those in which the groups exercise a large retarding influence. The most conspicuous of these is hydroxybenzamide while the amido group in the para position cuts the velocity down to less than one-

fourth of its normal value. The methoxy group stands alone in that it retards more when in the para than when in the ortho position, the velocities being 462 and 528, respectively. In the work with acid, the methoxy group in the para position was remarkable for its great influence, retarding almost as much as when in the ortho position, the velocities being 131 and 121, respectively. The third class of amides contains those having the nitro group or one of the halogens in the meta or para position. Those with the halogens are hydrolyzed two or three times as fast as benzamide, the meta being well ahead, while the nitro group quickens the reaction five and a half times when in the meta position and six and a half times in the para. The velocity here given for *p*-nitrobenzamide is calculated from that of the meta and the known relation of the meta and para at 90° C., as found in previous work. Paranitrobenzamide is less stable than the meta under the influence of both acids and alkalies. This and previous work goes to show that, with one exception to be noted presently, the hydrolysis of all the substituted benzamides proceeds regularly and in accordance with the equation assumed both in the presence of acids and alkalies. At the same concentration, baryta water acts usually some five or ten times as fast as hydrochloric acid. This is in contrast to statements based on merely qualitative experiments, such as that of Kolbe,[1] that orthoamidobenzamide is slowly saponified by caustic soda, easily by hydrochloric acid. As stated in the first article, I have boiled each of the amides studied with water and precipitated magnesium hydroxide for hours at a time and could never detect, either with litmus or with cochineal, even the slightest traces of ammonia in the distillate. In view of this, Engler's statement, "metabrombenzamide easily goes into acid with hot water," must be modified.[2] The results obtained with orthonitrobenzamide are not mentioned in the above as they seem so anomalous as to require special mention. In the one series given in the summary, it will be seen that the velocity decreases from 0.0522 to 0.0272. The shape of the curve given by plotting these results is also

[1] J. prakt. Chem. (2), **30**, 476.
[2] Ber. d. chem. Ges., **4**, 707.

striking. It starts up almost as well as some others, but gets flatter and flatter and approaches, as a limit, the 50 per cent line instead of the 100 per cent line. This led to a long series of experiments in which the heating was continued for much longer periods in order to trace the curve to its limit. The velocity is seen to slow down as 50 per cent decomposition is approached. Five hours gave 45.6 per cent; six hours, 48.6 per cent; seven hours, 48.3 per cent; eight hours, 50.1 per cent; and fifteen hours only 49.7 per cent, while twenty-five hours gave 48.8 per cent. The figure for eight hours is probably a little too high. Those for seven and twenty-five hours are too low, the deficiency, especially in the latter, being probably due to a slight escape of the ammonia from the little flask during the long heating. It is difficult to get rubber stoppers to remain tight at 100° C. Both had to be heated for several successive laboratory days. From the results given, it seems that orthonitrobenzamide, when boiled with baryta water, gives up half of the calculated amount of ammonia, and that prolonged boiling does not increase this amount. The results for the last series of experiments with orthonitrobenzamide were calculated by considering that there were just half as many molecules of the amide as were actually put in, that is k is put equal to

$$\log \frac{(A-2x)\frac{1}{2}B}{(B-2x)A} \quad \frac{2.3025}{(A-\frac{1}{2}B)t}.$$

After the first hour this gives a very satisfactory value for k which remains nearly constant until nearly 50 per cent is reached. These results led to a somewhat more thorough study of this reaction. The alkaline solution of the amide rapidly becomes red on heating until in a short time it assumes a beautiful clear red color. On acidifying the red solution, in which the reaction had been pushed to the limit, it takes on a yellowish turbid condition and a brilliant red, flaky precipitate is formed. This collects at the bottom and is inclined to assume a somewhat tarry condition. It is easily soluble in alkali, from which it can be again precipitated by acid. It is readily soluble in alcohol

Time in minutes.
Percentage of Ammonia Absorbed.
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
410
420
430
440
450
460
470
480
490
500
510
520
530
540
550
560
570
580
590
600

and comes down on the addition of water. If the alcoholic solution is allowed to evaporate, the substance is left as bright-red drops which on long standing solidify and then seem, when crushed, to be a mass of clear garnet-red crystals. I have obtained what seems to be the same substance by using caustic soda instead of baryta water. With caustic soda, containing even half a gram of hydrate to the cubic centimeter, it is impossible to get off more than half of the calculated ammonia even when boiled all day. With the most concentrated solutions, even less than half seems to come off, and the red substance, when precipitated, does not seem to be so pure as it does not so readily solidify. These facts are of interest as showing that at least one amide does not go into the corresponding acid when boiled with alkali. It is intended to investigate the red substance further.[1]

Many of the results here recorded are brought together at the end in the form of curves. The strange behavior of the *o*-nitrobenzamide is easily seen from an inspection of these. The form of the *o*-nitro curve is remarkable. It will be noticed that it crosses several of the others at quite sharp angles and approaches the 50 per cent line as an asymptote. At twenty-five hours or nearly three times the length of the curve as drawn, it is still only 50 per cent.

COLLEGE OF CHARLESTON,
CHARLESTON, S. C.,
June 28, 1900.

Contributions from the Sheffield Laboratory of Yale University.

LXXVII.—ON THE MOLECULAR REARRANGEMENT OF DISUBSTITUTED THIONCARBAMIC ESTERS: PHENYLIMIDOTHIOCARBONIC ACID DERIVATIVES AND THIOSEMICARBAZIDIC ESTERS.

BY HENRY L. WHEELER AND GUY K. DUSTIN.

In previous articles from this laboratory it has been shown that monosubstituted thioncarbamic esters, XNHCS.OR, react more or less readily with alkyl iodides, giving the isomeric

[1] Recent work has shown the red substance to contain some *o*-nitrobenzoic acid and another acid melting at about 261° C.

thiol derivatives, XNHCO.SR; and it was concluded that these ester amides are best represented by the normal form rather than by the pseudo structure, $XN{=}C\begin{matrix}SH\\OR\end{matrix}$. It seemed desirable, however, to determine whether or not the above-mentioned rearrangements were dependent on the presence of hydrogen; or, in other words, whether disubstituted xanthogenamides of the form XX'N—CS.OR would undergo a similar rearrangement, giving the thiol derivatives, the question being all the more interesting since it is customary to represent the thioamides and thioureas as reacting in their pseudoform with halogen compounds.

We find that the disubstituted thioncarbamic esters readily react with alkyl iodides, and that the N-methyl (I) and ethylthioncarbanilic esters undergo a rearrangement even more readily than the thioncarbanilic esters of the form $C_6H_5NHCS.OR$. It follows, therefore, that the pseudoform is not involved in these reactions, and that the rearrangement takes place, in general, as follows:

$$\text{(I)}\quad \begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!N{-}CS.OCH_3 \longrightarrow \begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!N{-}C(=S{-}I)\begin{matrix}CH_3\\OCH_3\end{matrix} \longrightarrow$$

$$\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!N{-}CO.SCH_3.$$

It is easy to distinguish whether a rearrangement has taken place or is complete in this series, since the thion derivatives are readily desulphurized by mercuric oxide when boiled in alcoholic solution, while the thiol derivatives are unaffected. The action takes place smoothly as follows:

$$\text{(II)}\quad CH_3.C_6H_5NCS.OR \longrightarrow CH_3.C_6H_5NCO.SR.$$

It was shown by Liebermann[1] that the sodium and silver salts of the thioncarbanilic esters react with alkyl halides in the following manner:

[1] Ann. Chem. (Liebig), **207**, 148.

(III) $C_6H_5N=C\begin{cases}SAg\\OC_2H_5\end{cases} \longrightarrow C_6H_5N=C\begin{cases}SC_2H_5\\OC_2H_5\end{cases}$.

Thus, the alkyl group attaches itself to sulphur and phenylimidothiocarbonic esters result. He examined the action of these compounds with sulphuric acid, aniline, and ammonia, at high temperatures. He found that the action of sulphuric acid gave aniline sulphate and thiocarbonic esters, thus showing the constitution of the compounds. With aniline, mercaptan was given off and carbanilide separated, while with ammonia (at 100°) decomposition products alone were obtained. He states that with hydrochloric acid alkyl chloride is evolved, on warming, and the compounds are converted back into phenylsulphurethane.

We have prepared some of these compounds in order to compare their behavior with that of the analogous acylimidothiocarbonic esters, $C_6H_5CO-N=C\begin{cases}SC_2H_5\\OC_2H_5\end{cases}$, and with that of anilinoimidothiocarbonic ester, the hydrazone of diethyl thiocarbonate, $C_6H_5NH-N=C\begin{cases}SC_2H_5\\OC_2H_5\end{cases}$. The results of the comparison show how strikingly the properties of compounds of similar structure are influenced by the character of groups.

It has been found that the benzoylimidothiocarbonic esters readily react with organic bases[1] while the hydrazone of ethyl thiocarbonate, which has precisely opposite properties, readily and smoothly reacts only with negative compounds, such as acyl chlorides, hydrochloric acid, thiobenzoic acid, etc.[2] We now find that the phenylimidothiocarbonic esters exhibit a behavior intermediate between the above, inasmuch as they are surprisingly unreactive with both acyl chlorides and with organic bases; in fact, they show a wide departure from most compounds which contain the imidoester grouping.

For example, it might be expected that the compounds of Liebermann would react with bases, giving the pseudourea

[1] Wheeler and Johnson: This JOURNAL, 24, 189.
[2] Wheeler and Barnes: *Ibid.*, 24, 60.

ethers of Stieglitz and Dains.[1] It was found, however, that aniline acts on these compounds only near its boiling-point, and then very slowly, and that carbanilide separates from the hot mixture, in crystalline form, before one-half of the mixture enters into reaction. On distilling, no pseudourea ether was found.

The hydrazone of thioethyl carbonate, like the isoanilides in general, reacts with acetyl and benzoyl chloride, in the cold with a violent evolution of alkyl chloride, while the compounds of Liebermann can be mixed with these chlorides without any evidence of reaction. Benzoyl chloride showed no signs of reacting with the following ester below 140°. On long continued heating, above this temperature, methyl chloride was slowly evolved and a benzoyl derivative was obtained. The reaction, in all probability, took place as follows:

(IV) $C_6H_5N{=}C\begin{matrix}SCH_3\\OCH_3\end{matrix} + Cl.COC_6H_5 =$

$$C_6H_5{-}N(C_6H_5CO){-}CO.SCH_3 + CH_3Cl.$$

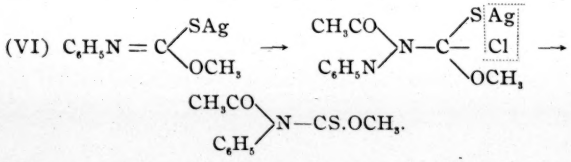
This action is probably analogous to that of hydrogen chloride, with which reagent the phenylimidothiocarbonic esters react smoothly and quantitatively, like the imidothiocarbonic esters in general, giving thiolcarbamic esters and not, as Lieberman states, regenerating phenylsulphurethane or the thion derivative. This mistake of Liebermann is probably due to the fact that ethyl thioncarbanilate and the corresponding thiol compound differ by about 1° in their melting-points, and may be easily mistaken for each other. However, the other members of these series differ more widely in their melting-points. The reaction with hydrogen chloride takes place with the formation of an addition-product, which decomposes with loss of alkyl chloride, as follows:

(V) $C_6H_5N{=}C\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix} \longrightarrow C_6H_5N(H)-C(SC_2H_5)(Cl)(OC_2H_5)$

[1] J. Am. Chem. Soc., **21**, 136.

In these and similar compounds it is almost invariably the group attached to oxygen that is evolved as alkyl chloride, and a thiol ester is formed. As another example of the comparative inertness of the phenylimidothiocarbonic acid grouping, we may add that no reaction was observed when benzoyl chloride was mixed with the silver salt of methyl thioncarbanilate suspended in benzene; and when the mixture was heated to 100° benzanilide was obtained.

With acetyl chloride the salt reacts in the cold. Silver chloride and an acetyl derivative are obtained as follows:



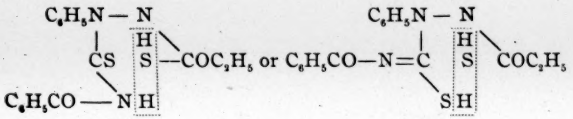
With the object of obtaining a new type of thiocarbamic esters, which perhaps may be called acylsulphosemicarbazidic esters, *i. e.* $C_6H_5CONHCSN(C_6H_5)$—NHCSOR, etc., since they contain the sulphosemicarbazide grouping,

$$—NH—CS—\overset{|}{N}—NH—,^{1}$$

we examined the behavior of acetyl and benzoylsulphocyanides with ethyl phenylthiocarbazinates. It was found that the thion ester behaves in a different manner from that of the thiol ester.

When acetyl- or benzoylsulphocyanide is mixed with ethyl phenylthioncarbazinate, hydrogen sulphide is evolved, even in the cold, and compounds of a very stable nature result. The reaction evidently takes place first by addition, with the formation of ethyl *c*-benzoyl-*b*-phenylsulpho-*a*-thionsemicarbazidate. This probably takes place according to one of the two following schemes, and hydrogen sulphide then separates as shown by the dotted lines, giving ring-formed compounds which are either triazole (VII) or thiobiazolone derivatives (VIII):

[1] For convenience in naming these compounds, sulphur in the urea radical is termed sulpho; when in the ester grouping it is called thion or thiol; and for general reference the compounds are referred to as thiosemicarbazidic esters.



(VII) (VIII)

Which ring is formed depends on whether the intermediate addition-product has the structure of a normal (VII) or pseudosulpho (VIII) semicarbazidic ester.

Freund and König[1] represent the action of isocyanphenyl chloride, $C_6H_5N{=}CCl_2$, on acylhydrazines in the same manner as that of phosgene, the products being viewed as imidoxybiazolines or compounds analogous to (VIII). The action in the present case might be expected to be similar. On the other hand, it has been shown by Marckwald[2] that compounds of this type are not desulphurized by metallic oxides while our material is desulphurized by silver nitrate; therefore, at present, we are inclined to represent these compounds as triazole derivatives, and assume the action to proceed as shown in (VII).

When acetyl- or benzoylsulphocyanide is mixed with ethyl phenylthiolcarbazinate no hydrogen sulphide is evolved, but the compounds unite directly to form an addition-product, as follows:

(IX) $C_6H_5CONCS + C_6H_5NH{-}NHCO.SC_2H_5 =$
$C_6H_5CONHCSN(C_6H_5){-}NHCO.SC_2H_5$.

These reactions sharply distinguish the thion- from the thiolcarbazinic esters, and the ease with which the former give ring compounds seems to indicate that the thion derivatives have the pseudo form. However, other facts, such as special arrangement, must also be considered in these cases.

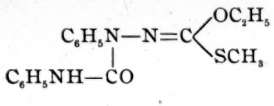
That the above formation of triazole derivatives (VII) is probably not caused by the phenylthioncarbazinic ester having the pseudo form is shown by the behavior of the latter with phenyl isocyanate. These compounds combine directly without giving off hydrogen sulphide, and the product has the

[1] Ber. d. chem. Ges., **26**, 2869.
[2] *Ibid.*, **25**, 3109; **27**, 617.

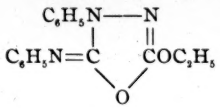
composition of the expected ethyl *c,b*-diphenyl-*a*-thionsemicarbazidate :

(X) $C_6H_5NCO + C_6H_5NH—NHCS.OC_2H_5 =$
$C_6H_5NHCON(C_6H_5)—NHCS.OC_2H_5.$

That the addition takes place to the nitrogen to which the phenyl group is attached, and that the grouping —NHCS. OC_2H_5 is present, is shown by the behavior of the compound with alkali and alkyl iodides. With methyl iodide and sodium methylate in the cold, diphenylureaimidothiolmethylethylcarbonate, the diphenylsemicarbazone of thiolmethylethylcarbonate, is formed (XI) ; while under the same conditions ethyl iodide gives a mixture of two compounds. These are thioldiethylcarbonicesterdiphenylsemicarbazone analogous to (XI) and a substance, free from sulphur, which appears to be the ring-formed compound α-ethoxy-α'-phenylimido-β'-phenyloxybiazoline (XII) :



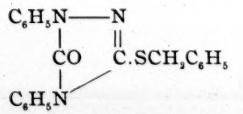
(XI)



(XII)

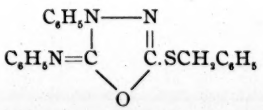
The compound (XII) is also formed on simply warming the diphenylthionsemicarbazidic ester with sodium ethylate.

On the other hand, with benzyl chloride the sole product obtained was not strictly analogous to either of the above derivatives ; it contained sulphur and agreed in composition with one of the following compounds :



(XIII)

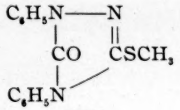
or



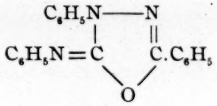
(XIV)

At present we have nothing but the properties of the compound to indicate to which of these series it belongs. The structure represented by formula (XIII) appears to be ex-

cluded, since Marckwald[1] has prepared a compound of this type, namely, 1,4-diphenyltriazolone-3-methylmercaptan (XV), and he has shown that this substance has decided basic properties, that it is soluble in acids, and that it gives a platinum double salt. Our compound, on the other hand, has no basic properties whatever. The nearest known analogues of a compound represented by formula (XIV) are the phenylimidooxybiazolines prepared by Freund and König[2]. The properties of their "*n*-phenyl-phenyl-phenylimidooxybiazolin" (*α*-phenyl-*α'*-phenylimido-*β*-phenyloxybiazoline, XVI) are closely similar to those of our compound, inasmuch as it is insoluble in water and is not affected by boiling with soda or hydrochloric acid, in which it is also insoluble:



(XV)



(XVI)

Moreover, it was found that the compound free from sulphur, mentioned above, has no basic properties, and therefore it appears that formulæ (XII) and (XIV) best represent the structure of the compounds in question. Further work on the structure of these compounds must be deferred to a later date, owing to the departure of one of us from this laboratory.

The behavior of the diphenylthionsemicarbazidic ester (X) with bases showed a wide departure from that of the benzoylthioncarbamic esters since derivatives of a pseudourea type were not obtained. When heated with aniline, or in fact when heated alone, carbanilide is the chief product. The properties of this type of esters are most closely related to those of the thioncarbanilic esters.

When the diphenylsemicarbazones of the thiolcarbonic esters (XI) are treated with hydrogen chloride, a reaction similar to that described in the case of the phenylimidothiocarbonic esters takes place (V above). The compounds obtained are identical with those prepared by adding phenyl isocyanate to

[1] Ber. d. chem. Ges., **25**, 3111.
[2] *Loc. cit.*

the phenylthiolcarbazinic esters, in which case again no hydrogen sulphide is evolved; the addition therefore takes place in a similar manner to that shown in (X).

In addition to the above we have investigated the action of some thion and thiol salts of carbonic and carbamic acids with ethyl chlorcarbonate, and we find that no two of these salts behave alike. For example, Bender's salt, to which the structure $C_2H_5OCO.SK$ is assigned, reacts in two ways as follows, chiefly according to (XVII):

XVII. $C_2H_5OCO.SK + ClCO.OC_2H_5 = C_2H_5OCO.OC_2H_5 + KCl + COS.$

XVIII. $C_2H_5OCO.SK + ClCO.OC_2H_5 = C_2H_5O.CO.SC_2H_5 + KCl + CO_2.$

The products are diethyl carbonate, diethyl thiolcarbonate, carbon oxysulphide, carbon dioxide, and potassium chloride.

Potassium xanthate, $C_2H_5OCS.SK$, reacts with 1 molecule of chlorcarbonic ester in an extremely complicated manner. We identified the presence of five different oils in the reaction-product. These were carbon disulphide, ethyl carbonate, diethyl thiocarbonate, xanthogenic ester, and Welde's[1] "disulphodicarbothionsäurediäthyl ester."

We were unable to obtain the sodium salt of thionethylcarbonate, $C_2H_5OCS.ONa$, described by Klason.[2] In this respect our experience coincides with that of Bergreen,[3] whose results on the action of thiophosgene on sodium ethylate we are able to confirm.

Ammonium dithiocarbanilate, $C_6H_5NHCS.SNH_4$, gave, with 1 molecule of chlorcarbonic ester, chiefly thiocarbanilide, phenylsulphocarbamide, and phenyl mustard oil; while the phenylhydrazine salt of dithiophenylcarbazinic acid,

$$C_6H_5NH—NHCSSH.H_2N—NHC_6H_5,$$

gave a good yield of Heller's[4] ethyl phenylcarbazinate. The

[1] J. prakt. Chem. [2], **15**, 45.
[2] Ber. d. chem. Ges., **20**, 2384.
[3] *Ibid.*, **21**, 346.
[4] Ann. Chem. (Liebig), **263**, 278.

latter had all the properties mentioned by Widman.[1] Besides this an unpromising green tar was formed.

EXPERIMENTAL PART.

Methyl Methylthioncarbanilate, $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!N\!-\!CS.OCH_3$. — The chloride, $C_6H_5(CH_3)NCS.Cl$, was prepared by the method of Billeter.[2] In two experiments 15 grams of thiophosgene gave the theoretical yield of the chloride. This was added to a solution of sodium methylate in methyl alcohol when a reaction took place at once; it was warmed for a half hour on the water-bath, then treated with water, extracted with ether, and distilled at 19 mm. pressure, whereupon it boiled mostly from 151°–152°. It was a colorless oil which did not solidify on cooling, and a nitrogen determination gave:

	Calculated for $C_9H_{11}NOS$.	Found.
N	7.7	7.3

Methyl Methylcarbanilate, $C_6H_5(CH_3)NCO.OCH_3$, was formed on boiling the above thion ester (12 grams) with an excess of mercuric oxide in alcoholic solution. It was obtained as an oil which distilled for the most part from 117° to 119° at 16 mm. pressure, and a nitrogen determination gave:

	Calculated for $C_9H_{11}NO_2$.	Found.
N	8.48	8.71

Ethyl Methylthioncarbanilate, $C_6H_5(CH_3)NCS.OC_2H_5$.— This was prepared from the above chloride in the same manner as the methyl ester. It formed a colorless oil which boiled mostly from 145° to 150° at 18 mm. pressure. It refused to solidify, and a nitrogen determination gave:

	Calculated for $C_{10}H_{13}NOS$.	Found.
N	7.1	6.9

It may be boiled with concentrated hydrochloric acid without change.

[1] Ber. d. chem. Ges., **28**, 1927.
[2] *Ibid.*, **20**, 1631.

Methyl N-Ethylthioncarbanilate, $C_6H_5(C_2H_5)NCS.OCH_3$.—This compound was prepared in the same manner as the corresponding ethyl ester.[1] The crude product was obtained as an oil which was distilled at 18 mm. pressure, whereupon the most of the material boiled from 148° to 149°. It then solidified and, on crystallizing from petroleum ether, beautiful, colorless, five-sided plates separated, melting from 41° to 42°. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}NOS$.	Found.
N	7.17	7.50

Methyl Methylthiolcarbanilate, $C_6H_5(CH_3)NCO.SCH_3$.—This compound is easily obtained when the thion ester is heated with methyl iodide for four hours from 103° to 106°. On cooling, a small amount of crystalline material separates, which appears to be trimethylphenylammonium iodide. The rest of the product, when distilled at 16 mm. pressure, boils for the most part from 140° to 142°. The material then solidifies, and when crystallized from alcohol, in which it is readily soluble, it melts at 46°. It forms colorless plates which, on analysis, gave:

	Calculated for $C_9H_{11}NOS$.	Found.
N	7.77	7.38

This ester has been obtained in another manner by Bertram.[2] He states that it melts at 54°. Our material was free from the thion ester since it was not desulphurized on boiling with mercuric oxide.

Ethyl N-Methylthiolcarbanilate, $C_6H_5(CH_3)NCO.SC_2H_5$.—The thion ester was heated in a closed tube for a number of hours at 100° with ethyl iodide, then, on distilling, an oil was obtained which boiled from 160° to 163° at 19 mm. pressure. On cooling, this solidified and melted from about 12°–13°. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}NOS$.	Found.
N	7.17	7.38

[1] Billeter and Strohl: Ber. d. chem. Ges., **21**, 104.
[2] Ber. d. chem. Ges., **25**, 53.

Methyl N-Ethylthiolcarbanilate, $C_6H_5(C_2H_5)NCOSCH_3$. — This was obtained as an oil by heating the thion ester with methyl iodide. It boiled from 148° to 149° at 17 mm. pressure, and it did not solidify on cooling. A nitrogen determination gave results agreeing with the calculated. The record of this determination is lost. It was free from the thion ester, since it was not desulphurized by boiling in alcoholic solution with mercuric oxide.

Ethyl N-Dimethylthioncarbamate, $(CH_3)_2NCS.OC_2H_5$.—The action of alcoholic dimethylamine was tried on xanthogenic ester in order to see if the action in the case of aliphatic amines is the same as that of ammonia and phenylhydrazine. It was found that these substances react less smoothly than when ammonia is used. In the present case, after the above mixture was allowed to stand about two weeks, the product was an oil which distilled, for the most part, at 203°–205°. A nitrogen determination indicated the presence of xanthogenic ester. The material was then treated with alcoholic potash and allowed to stand for twenty-four hours, whereupon, on distilling, it boiled from 205° to 206°, and a nitrogen determination gave 9.1 per cent of nitrogen instead of 10.5.

Diamylamine reacted even less smoothly with xanthogenic ester. When these substances were mixed and allowed to stand for four or five days, then heated for some time on the steam-bath, mercaptan was given off, but the product, when distilled, gave no constant boiling-point.

Dimethyl Phenylimidothiolcarbonate, $C_6H_5N{=}C\begin{matrix}SCH_3\\OCH_3\end{matrix}$. — This was prepared by treating methyl thioncarbanilate in methyl alcohol with sodium methylate and methyl iodide. On distilling, the product boiled at 133° at 17 mm. pressure and was a yellow oil with a peculiar odor. When this was treated with hydrogen chloride in solution in benzene, no precipitate was obtained, the solution evolved heat, and methyl chloride escaped. On evaporation, an oil was obtained which solidified to a mass of colorless crystals, and when crystallized from petroleum ether, fine, long needles were obtained, melting from 83° to 84°. This material was identical in every re-

spect with *methyl thiolcarbanilate*, $C_6H_5NHCO.SCH_3$. The thion ester melts at 97°.[1]

When the above imidothiolcarbonic ester was heated with aniline in an oil-bath at 180°–190° for several hours, carbanilide crystallized out from the hot mixture. The heating was then stopped and the mass filtered and the oil distilled at 17 mm. pressure, whereupon about one-half of the product boiled from 82°–131°, and the remainder from 131°–140°. It follows from this that little or no methylisocarbanilide was present, since the isourea ethers boil near 200° at the above pressure.[2] On heating this carbonic ester derivative with diisobutylamine for several hours in an oil-bath from 145°–150° no effervescence took place and little or no mercaptan was evolved. This deportment with bases is in striking contrast with the behavior of the benzoylimidothiocarbonic acid derivatives which readily react at a much lower temperature.[3]

Methyl Benzoylthiolcarbanilate, $C_6H_5CO(C_6H_5)N-CO.SCH_3$. —On mixing 2 grams of the above dimethyl carbonate with 1 molecular proportion of benzoyl chloride and heating, no action was observed below 140°. At this temperature methyl chloride was evolved, and on maintaining the bath at 150° for several hours a slow evolution of gas was noticed. On cooling and crystallizing the residue from petroleum ether, well-crystallized needles or prisms were obtained melting at about 93°. When this was mixed with methyl thioncarbanilate (melting-point 97°) the mixture melted at about 83°. A nitrogen determination gave :

	Calculated for $C_{15}H_{13}NO_2S$.	Found.
N	5.16	5.75

That this material is a benzoyl derivative was shown by warming it with aniline on the water-bath when benzanilide was obtained.

When dimethyl phenylimidothiolcarbonate was mixed with acetyl chloride no action whatever was observed, while the analogous ethyl phenylimidoformate, $C_6H_5N=CHOC_2H_5$ reacts violently with acetyl chloride.[4]

[1] Orndorff and Richmond : This JOURNAL, **22**, 462.
[2] Stieglitz, also Dains : *Loc. cit.*
[3] Wheeler and Johnson : This JOURNAL, *loc. cit.*
[4] Wheeler and Walden : This JOURNAL, **19**, 134.

Methyl Acetylthioncarbanilate, $CH_3CO.(C_6H_5)NCS.OCH_3$.—The silver salt of methyl thioncarbanilate was prepared in the usual way by means of sodium hydrate and alcoholic silver nitrate. It forms an amorphous gray precipitate. When this (17 grams), after drying, was treated with acetyl chloride in benzene, a reaction took place in the cold, and on evaporating the benzene and crystallizing the residue from dilute alcohol, colorless crystals separated melting from 47°–49°. A nitrogen determination gave :

	Calculated for $C_{10}H_{11}NO_2S$.	Found.
N	6.69	6.71

The material was desulphurized on boiling in alcoholic solution with mercuric oxide, showing the presence of the thion group. When this compound was warmed with aniline it gave methyl thioncarbanilate and acetanilide.

Diethyl Phenylimidothiolcarbonate, $C_6H_5N=C\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}$.—We prepared this ester according to the directions of Liebermann[1] except that alcoholic solutions were used instead of aqueous, as otherwise it frequently happens that a product is obtained which is completely decomposed when distilled. This ester was found to boil from 157°–160° at 21 mm. pressure.

When this oil was treated with hydrogen chloride in benzene no precipitate was obtained. On evaporating and crystallizing the residue from dilute alcohol, needles separated which melted at about 69°. That this material was ethyl thiolcarbanilate and not the thion compound was shown by mixing a portion with each of these substances. When mixed with the thiol ester melting from 69°–70° the mixture melted unaltered at the same temperature ; when mixed with the thion ester melting at about 71° it melted below 60°.

Phenylimidothiolisoamylethylcarbonate, $C_6H_5N=C\begin{matrix}SC_5H_{11}\\OC_2H_5\end{matrix}$. —This oil was prepared by Mr. T. B. Johnson in order to compare its behavior towards hydrogen chloride with that of

[1] Ann. Chem. (Liebig), **207**, 150.

the analogous compound, $C_6H_5CON=C\begin{matrix}SC_5H_{11}\\OC_2H_5\end{matrix}$, which latter gives a thion and not the thiol ester. The oil was made by treating the sodium salt of ethyl thioncarbanilate in alcohol with amyl bromide. When the mixture no longer gave an alkaline reaction, water was added, and the product extracted with ether. On attempting to distil the oil under reduced pressure it decomposed. A portion of the crude material was saturated in benzene with hydrogen chloride, whereupon, on evaporating and crystallizing the residue from alcohol, long, colorless needles were obtained which melted at 66° and had all the properties of isoamyl thiolcarbanilate.

Action of Acetylrhodanide on Ethyl Phenylthioncarbazinate.—Two grams of the latter and 1 gram of the former were mixed together and gently warmed, whereupon hydrogen sulphide was evolved; when this ceased and the product was crystallized from 95 per cent alcohol bunches of colorless needles separated, which melted from 93°–94°. A nitrogen determination gave the following result:

	Calculated for $C_{12}H_{13}N_3O_2S$.	Found.
N	15.96	16.54

For reasons stated in the introduction, this product is in all probability 1-phenyl-3-ethoxy-4-acetyl-5-sulphotriazolone.

Action of Benzoylrhodanide on Ethyl Phenylthioncarbazinate.—Two grams of the carbazinic ester were mixed with 1.4 grams of the rhodanide and warmed, after hydrogen sulphide ceased being evolved, the product was crystallized from alcohol, whereupon flattened prisms melting from 136°–138° were obtained. These, on analysis, gave:

	Calculated for $C_{17}H_{15}N_3O_2S$.	Found.
N	12.9	12.6

The analytical result agrees with the calculated for 1-phenyl-3-ethoxy-4-benzoyl-5-sulphotriazolone. This compound is exceedingly stable, since it was found that it can be boiled with hydrochloric acid, concentrated ammonia, strong potash, aniline; and also with benzoyl chloride and be recovered un-

altered. An alcoholic solution of silver nitrate desulphurizes it on boiling, which fact indicates that the substance is a triazole derivative and not a biazolone.

c-Acetylsulpho-b-phenyl-a-semicarbazidicthiolethyl Ester, $CH_3CONH—CS—N(C_6H_5)—NHCO.SC_2H_5$.—When 1 gram of thiolphenylcarbazinic ethyl ester was mixed with 0.5 gram of acetylrhodanide in benzene solution and the whole was warmed, no hydrogen sulphide was noticeable. On standing, long prisms separated, melting at 145°. These were difficultly soluble in benzene, and an analysis gave :

	Calculated for $C_{12}H_{15}N_3O_2S_2$.	Found.
N	14.14	14.28

When this product is heated to 160°, mercaptan is evolved.

c-Benzoylsulpho-b-phenyl-a-semicarbazidicthiolethyl Ester, $C_6H_5CONH—CS—N(C_6H_5)—NHCO.SC_2H_5$. — Benzoylrhodanide and ethyl thiolphenylcarbazinate readily combine in benzene solution. The product separates from benzene in colorless needles or prisms melting at 148°–150°. A nitrogen determination gave :

	Calculated for $C_{17}H_{17}N_3O_2S_2$.	Found.
N	11.69	12.13

c,b-Diphenyl-a-semicarbazidicthionethyl Ester, $C_6H_5NH—CO—N(C_6H_5)—NHCS.OC_2H_5$.—Ethyl thionphenylcarbazinate dissolves in the calculated quantity of phenyl isocyanate, when the mixture is gently warmed, and then solidifies. On crystallizing the material then from alcohol colorless prisms, melting from 114°–115°, separate. Nitrogen determinations gave the following results :

	Calculated for $C_{16}H_{17}N_3O_2S$.	Found.	
		I.	II.
N	13.0	13.09	13.01

When this material was heated with aniline, carbanilide was obtained which was identified by its properties and also by a nitrogen determination.

c-b-Diphenyl-a-semicarbazidicthiolethyl Ester, $C_6H_5NH—CO—N(C_6H_5)—NHCO.SC_2H_5$, formed by adding phenyl isocyanate to the thiolcarbazinic ester, crystallizes in

small, spear-shaped plates, which are quite difficultly soluble in alcohol and which melt at 156°. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3O_2S$.	Found.
N	13.0	13.2

These esters are soluble in alkali and on boiling are decomposed.

ε,b-Diphenyl-a-semicarbazidicthiolmethyl Ester, $C_6H_5NHCO—N(C_6H_5)—NHCO.SCH_3$.—This was prepared in a similar manner to the above ethyl ester in order to determine whether it could be converted into the "diphenylimidobiazolonyl-μ-methylsulfid," (1,4-diphenyltriazolone-3-methylmercaptan of Marckwald),[1] the nearest analogue of the ring-formed compounds described in this paper, and thus decide whether the compounds in question are triazol derivatives or thiobiazolones. Theoretically, all that is required is the removal of water from the above ester in the same manner as hydrogen sulphide separates in formula VII, but attempts to do this were without success. The ester crystallizes from alcohol in small plates, which melt at 186°, and it is identical with the compound prepared from diphenylureaimidothiolmethylethylcarbonate (see below) and hydrogen chloride. When heated to its melting-point it decomposes, slowly giving off mercaptan and phenyl isocyanate. It dissolves in concentrated sulphuric acid and is precipitated unaltered by water. It can be boiled with acetic anhydride, from which it crystallizes unaltered in prisms. It is insoluble in concentrated boiling hydrochloric acid, but it dissolves readily in alkali. When the alkaline solution was boiled an inflammable gas was given off and, on cooling, needles separated. These melted at 161°, after crystallization from alcohol, and were insoluble in hydrochloric acid. This was not the compound sought for, and therefore it was not further examined.

ε, b-Diphenyl-a-semicarbazidicthiolbenzyl Ester, $C_6H_5NHCO—N(C_6H_5)—NHCO.SCH_2C_6H_5$.—Phenyl isocyanate unites readily with thiolphenylcarbazinicbenzyl ester in benzene solution. The product is readily soluble in benzene

[1] Ber. d. chem. Ges., **25**, 3111.

and hot alcohol, difficultly soluble in cold alcohol, and insoluble in water. It crystallizes in small bunches of flattened prisms or plates, which melt at about 150°. A nitrogen determination gave:

	Calculated for $C_{21}H_{19}N_3O_2S$.	Found.
N	11.1	10.8

Thiolmethylethylcarbonicesterdiphenylsemicarbazone, $C_6H_5NH—CO—N(C_6H_5)—N=C\begin{matrix}SCH_3\\OC_2H_5\end{matrix}$, was prepared by adding ice-cold sodium methylate and methyl iodide to the above diphenylsemicarbazidicthionethyl ester. After remaining in the cold for two hours the action was complete, whereupon water was added, and the product extracted with ether. On crystallizing from alcohol, lozenge-shaped crystals were obtained which melted at 108°–109°, and a nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3O_2S$.	Found.
N	12.7	12.6

When this substance, dissolved in benzene, was treated with hydrogen chloride, ethyl chloride was evolved and the above-described thiolmethyl ester, which melts at 186°, was obtained.

Thioldiethylcarbonicesterdiphenylsemicarbazone, $C_6H_5NHCON(C_6H_5)—N=C\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}$, was obtained when a mixture of ethyl bromide, sodium ethylate, and the above thionsemicarbazidicethyl ester was allowed to stand at ordinary temperatures for several hours. On crystallizing the product from dilute alcohol, needles were obtained which melted at about 111°. The yield is poor, as under these conditions a compound free from sulphur is also formed. The compound melting at 111° gives the above-described ethyl thiolsemicarbazidate with hydrogen chloride, a reaction which easily serves to identify it. It is readily soluble in alcohol and benzene, difficultly in petroleum ether, and insoluble in water.

α-Ethoxy-α-phenylimido-β'-phenyloxybiazoline, $C_6H_5N{-}{-}{-}N$ / $C_6H_5N{=}C{-}O{-}COC_2H_5$.—This appears to be the compound free from sulphur that accompanies the above carbonic ester derivative. It was also obtained when 2 grams of *c,b*-diphenyl-*a*-semicarbazidicthionethyl ester was boiled in alcohol with sodium ethylate for two hours. Water then precipitated the compound, which crystallized in fine, long, slender prisms from alcohol. It melted at 86°, and a nitrogen determination gave :

	Calculated for $C_{16}H_{15}N_3O_2$.	Found.
N	14.9	14.6

α-Benzylmercapto-α'-phenylimido-β'-phenyloxybiazoline, $C_6H_5N{-}{-}{-}N$ / $C_6H_5N{=}C{-}O{-}CSCH_2C_6H_5$.—When the above diphenylsemicarbazidicthionethyl ester is dissolved in aqueous alkali and warmed with benzyl chloride, an oil is obtained which, on cooling, solidifies. On crystallizing from alcohol, the material separates in the form of colorless needles melting at 110°–112°. This contains sulphur, and nitrogen determinations gave :

	Calculated for $C_{21}H_{17}N_3OS$.	Found.	
		I.	II.
N	11.6	11.5	11.5

This compound is insoluble in boiling water and hydrochloric acid, concentrated or dilute. It is insoluble and gives off no mercaptan on boiling with strong potash. The properties have nothing in common with Marckwald's 1,4-diphenyltriazolone-3-methylmercaptan, and therefore they indicate that this compound is not a triazol derivative. When the substance is heated with phosphorus pentachloride hydrogen chloride is evolved, indicating decomposition.

The Behavior of Bender's Salt, $C_2H_5OCO.SK$, with Ethyl Chlorcarbonate.—When 55 grams of the salt were treated with the calculated quantity of ethyl chlorcarbonate, the latter being dropped slowly on the salt, an energetic reaction took place and carbon dioxide and carbon oxysulphide were

evolved. The latter was identified by standing over water when hydrogen sulphide was formed. On distilling the product it boiled from 125°–217°(?). The greater portion came over from 125°–144°; this, when redistilled, gave 20 grams of oil boiling at about 126°, which proved to be ethyl carbonate. The higher-boiling portions gave urethane, carbamide, and mercaptan when treated with alcoholic ammonia, indicating the presence of thiolethyl carbonate.

Potassium Xanthate, $C_2H_5OCS.SK$, and Ethyl Chlorcarbonate.—When 55 grams of potassium xanthate and 37 grams of ethyl chlorcarbonate were allowed to react and the gas that was evolved was passed into alcoholic potash, no test for carbon oxysulphide was obtained. It appeared to consist entirely or, at any rate for the most part, of carbon dioxide. On distilling the resulting oil, 5 grams boiling below 161°, 31 grams from 161°–181°, and 10 grams from 181°–186° were collected.

It was found on redistilling these fractions that they boiled through a much wider range and that no definite boiling-point could be obtained. In the first portions, carbon disulphide (45°–120°) and ethyl carbonate (126°–130°) were identified. On treating portions boiling from 130° to above 200° with alcoholic ammonia, ammonium sulphocyanide, ammonium carbonate, ammonium sulphide, and xanthogenamide were obtained, thus indicating the presence of thionethyl carbonate, xanthogenic ester, and Welde's[1] compound, $S(CS.OC_2H_5)_2$.

Ammonium Dithiocarbanilate, $C_6H_5NHCS.SNH_4$, and Ethyl Chlorcarbonate.—When the dry salt was treated with chlorcarbonic ester in molecular proportions, an energetic reaction took place, carbon oxysulphide was evolved, and a semisolid residue was obtained. On treating this with alkali and warming, little or nothing dissolved except ammonium chloride (absence of ethyl thioncarbanilate). The material had a strong odor of phenyl mustard oil, which was removed by treating with ether. On crystallizing from alcohol two substances were obtained, one melting at 150° (plates) which proved to be carbanilide, the other melting at 154° (prisms), which on analysis gave 18.2 per cent of nitrogen, while the calculated for monophenylthiourea is 18.4 per cent.

[1] *Loc. cit.*

The phenylhydrazine salt of dithiophenylcarbazinic acid and ethylchlorcarbonate react in benzene solution without evolution of gas. On filtering from phenylhydrazine hydrochloride, evaporating the benzene solution, and then crystallizing the residue from a mixture of benzene and petroleum ether, colorless prisms were obtained which melted from 76°–77°. A nitrogen determination gave:

	Calculated for $C_6H_5NH-NHCO_2C_2H_5.H_2O$.	Found.
N	14.1	14.5

The solution in sulphuric acid gave an intense red color with ferric chloride, the compound agreeing in properties with those described by Widman for ethyl phenylcarbazinate.

NEW HAVEN, CONN., May 14, 1900.

Contribution from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXVI.—THE DETECTION OF METHYL ALCOHOL IN MIXTURES.

BY S. P. MULLIKEN AND HEYWARD SCUDDER.

In a recent article by E. Jandrier[1] it is stated that a test for methyl alcohol described by us[2] in an earlier number of this JOURNAL and based on the oxidation of the alcohol to formic aldehyde, followed by condensation of the latter to a colored derivative of resorcine, is unreliable, because it is also given by acrolein and is interfered with by the presence of furfurol. To remedy these defects in our method Jandrier recommends that gallic acid be employed instead of resorcine as the reagent for formic aldehyde, he having found in an earlier investigation[3] that the color reaction obtained by the use of gallic acid is much more delicate and less likely to be obscured by colorations occasioned by the simultaneous presence of other aldehydes.

A careful examination by the authors of this modification of their test soon proved that its use for the purpose proposed is entirely inadmissible, and this despite the fact that gallic

[1] Ann. Chim. Anal. App. **4**, 156; Centrbl., 1899, I, 1296 (abstract).

[2] This JOURNAL, **21**, 266.

[3] Barbier and Jandrier: Ann. Chim. Anal. App., **1**, 325; **Analyst, 21, 295 (abstract).**

acid is actually, as claimed, a better reagent for the detection of formic aldehyde than is resorcine! The explanation of this paradox will be made apparent by a consideration of certain facts that have lately come to our knowledge while studying the partial oxidation by hot copper oxide of a considerable number of organic compounds.

The means chosen for oxidizing methyl alcohol to formic aldehyde detailed in our first paper, was the very simple one of plunging a short, closely-wound spiral of light copper wire, previously heated to redness and superficially oxidized, into the solution to be tested. Special emphasis was placed on the condition that "A concentrated spirit should always be diluted with at least three or four volumes of water before oxidation." It was also particularly noted that 1 drop of 0.5 per cent resorcine solution was the quantity of reagent that should be added for every 3 cc. of all solutions originally containing more than 0.1 per cent of methyl alcohol. These minute specifications were necessary, partly because it had been found that absolute ethyl alcohol, when directly oxidized without previous dilution, would, if afterwards largely diluted with water, give a very faint color reaction resembling that caused by formic aldehyde. This color was, however, noticed only when the weight of resorcine added to a given volume of solution was many times less than that usually employed, and it first made its appearance after several hours instead of within a few minutes, as usually happened with solutions that really contained methyl alcohol. The conditions necessary for the production of this color from ethyl alcohol were so unusual, its intensity was so slight, and its cause so obscure, that no account of it was included in our first paper. A more suggestive observation was made by us at the same time with reference to the use of caseine, of which we wrote :[1] "Caseine is not a suitable reagent for methyl alcohol tests, because the oxidation-products of ethyl alcohol yield with it the same blue color as formic aldehyde; though singularly enough solutions of pure acetaldehyde do not give this result."

After the gallic acid reaction for formic aldehyde had been brought to our attention, we endeavored to verify the advan-

[1] *Loc. cit.*

tages claimed for it in the detection of methyl alcohol. For our purpose it was found best to employ the reagent very nearly in the manner recommended by Istrati.[1] 0.2 cc. of a saturated solution of gallic acid in pure ethyl alcohol was mixed with a few drops of the oxidized alcoholic solution to be tested, diluted to 2 cc., and the mixture carefully run down the side of an inclined test-tube containing a few cubic centimeters of concentrated sulphuric acid. At the line of contact between the two liquids a yellow zone, almost immediately turning green, makes its appearance, if the solution contains formic aldehyde. Above and below the green zone, blue rings then rapidly develop. If other substances which give color reactions are also present, the upper layer will vary in color, but the green and the lower blue ring will still appear beneath. The colors are pure and characteristic, and are not obscured by the presence of other aldehydes. Having familiarized ourselves with these phenomena, it was with considerable surprise that we found the oxidation-products obtained in the usual way from the purest procurable ethyl, propyl, isopropyl, secondary butyl, tertiary butyl, and normal butyl alcohols, ethylene glycol, glycerin, acetaldehyde, paraldehyde, ethyl ether, acetone, pinacone, and acetic acid, all gave distinct green and blue rings with gallic acid.

The total failure of the gallic acid test to distinguish the substances enumerated from methyl alcohol, as well as the anomalous results noted in our earlier experiments with the oxidation-products from concentrated ethyl alcohol when tested with a trace of resorcine or with caseine, are susceptible of only two simple explanations. Either all the apparently pure compounds oxidized must have contained methyl alcohol or methyl derivatives as impurities, or the list of compounds which may give traces of formic aldehyde upon oxidation with copper oxide is a very much longer one than has hitherto been suspected. The hypothesis that methyl alcohol in small

[1] Analyst, **23**, 230 (abstract) (1898). Istrati's original memoir on the color reactions between aldehydes and phenols (Buletinul Societatei de Sciinte, Bucuresci, vii (2), 163–170) which was made accessible to us through the kindness of M. Jandrier, forms a continuation of the earlier studies of Barbier and Jandrier. Another still earlier research on the value of phenols for the detection of aldehydes, mention of which was also unintentionally omitted in our first paper, is by Nickel (Fres. Zeit. (1889), 249).

quantities may be formed along with ethyl alcohol in alcoholic fermentations is perhaps not unworthy of a more thorough investigation than it has received. Trillat claims to have detected traces of it in some genuine brandies. But it is, nevertheless, highly improbable that all the cases which have been noted by us in which formic aldehyde reactions were obtained from the oxidation-products of the many presumably pure substances taken for our experiments can be explained in this way, and we inclined strongly, from the first, to the acceptance of the second explanation, the probability of which has since become a certainty in consequence of a supplementary quantitative investigation conducted by one of the authors with the assistance of Messrs. Brown and French, an account of which will follow later in this JOURNAL.

The logical justification for adhering to the use of resorcine in the test for methyl alcohol lies, then, in the presumption that no common organic compound that could occur in such solutions as are provided for by the method (with the exception of methyl esters or ethers), will furnish enough formic aldehyde, or other substance, exhibiting a similar behavior, when treated with due regard to the detailed directions to give a rose-red ring and flocks. This presumption is a sufficiently well-founded one, when all the precautions that will be given further on in this paper are observed. The gallic acid and caseine tests, on the contrary, must be rejected, because they are so delicate that formic aldehyde may be detected by their use in nearly any organic solution that has been partially oxidized by means of a copper spiral.

Since the publication of our first paper we have had occasion to apply the resorcine test for methyl alcohol to a great variety of mixtures, and as a consequence of the fuller knowledge of the imperfections of the method thus gained, we are now in a position to suggest certain improvements in the original procedure, which, we believe, will considerably augment its practical usefulness. Analysts are, as a rule, too prone to ignore the fact, that the *absolute* identification of any compound by the use of some single specific reaction is an unattainable end when really unknown mixtures are dealt with. Specific qualitative tests are of great value when judiciously

employed ; but each new mixture must be considered by itself, and whenever there is reason to suspect the presence of substances which may interfere with the test selected, means for their removal must first be devised. The list of compounds whose presence may mask the color reactions given by phenols with formic aldehyde is a long one, and includes bodies which are likely to be met with in such important mixtures as the commercial tinctures, extracts, varnishes, alcoholic beverages, and solvents. While it would be feasible to formulate quite definite rules of procedure for the detection of methyl alcohol in any limited group of mixtures, it will be more profitable here to make certain general suggestions that will be of service in the solution of a variety of special problems.

The following precautions should always be observed :

(*a*) Use for the test only that part of any mixture that can be completely distilled at a temperature between 50° and 100°, and which, after distillation, gives a clear colorless solution when shaken with two or three volumes of water.

(*b*) Make a blank experiment, before oxidation with the copper spiral, by pouring 2 cc. of a clear aqueous solution of the distillate of proper boiling-point, to which 1 drop of 0.5 per cent resorcine solution has been added, so as to form a layer upon concentrated sulphuric acid in a test-tube. If a precipitate or a colored ring make its appearance, the solution requires further preliminary treatment.

(*c*) Do not test without preliminary treatment any solution that is known or suspected to contain phenols, alkaloids, or organic bases.

The reasons for these precautions are obvious. Many organic compounds give colorations with sulphuric acid alone ; others, including nearly all aldehydes and many bases, condense easily with resorcine under the conditions of the test to insoluble or intensely colored products. Other phenols besides resorcine, and many bases, will, if present, react with any formic aldehyde that may arise by oxidation with the wire, and thus prevent or obscure the appearance of the characteristic rose-red ring.

Methyl alcohol may be separated easily from most coloring-matters, oils, resins, sugars, glycerine, and glycols, by a sim-

ple distillation; from phenols and acids by distillation from an aqueous solution containing caustic alkali; from bases by distillation from aqueous solutions strongly acidified with a dilute mineral acid. When small quantities of methyl alcohol are extracted from insoluble organic mixtures by shaking out with water, it is to be remembered that the methyl alcohol will tend to concentrate in the first part of the aqueous distillates obtained from such solutions, and that various aldehydes, phenols, and bases may pass over with it on account of their volatility with steam, and will have to be removed afterwards.

When the preliminary blank experiment (*b*) gives a coloration or precipitate, and the solution gives aldehydic reactions with ammoniacal silver nitrate and with Schiff's rosaniline-aldehyde reagent, take 12 cc. of the alcoholic distillate, which, if concentrated, must first have been diluted so as to contain at least 75 per cent of water; place in a small firmly stoppered bottle with 3 grams of resorcine and 1 cc. strong sulphuric acid, and heat for two hours in a water-bath at 70°–80°. Cool, dilute the solution to 50 cc. with water, distil off 5 cc., and test the distillate for methyl alcohol in the usual manner. Large quantities of aldehydes may be held back by resorcine in this way, though, when the mixture consists mainly of aldehydes, more resorcine and longer heating will be required. An analogous method for accomplishing this same result, which employs aniline and phosphoric acid instead of resorcine and sulphuric acid, was proposed by Allen and Chattaway[1] for use in the analysis of whiskies. We have used both these methods with success npon mixtures containing as high as 50 per cent of furfurol and other aldehydes, thus meeting the chief objection which Jandrier has raised against our procedure.

A more difficult, but practically far more important, problem than that of removing aldehydes from the original mixtures, had to be faced, when we sought to discover some simple means for taking away the acetaldehyde which is always formed together with formic aldehyde when mixtures containing both ethyl and methyl alcohols are oxidized. The

[1] Analyst, 16, 102.

most that could be previously claimed for the test with resorcine in such mixtures was, that "One part of methyl alcohol may be detected without great difficulty in the presence of five parts of ethyl alcohol." A simple and fairly satisfactory way out of this difficulty was, however, found.

Acetaldehyde is easily and completely expelled from aqueous solutions by persistent boiling in a vessel provided with some condensing arrangement that will prevent too rapid loss of water vapor. Dilute solutions of formic aldehyde, on the contrary, lose their aldehyde very slowly under this treatment, it being firmly held, partly in a polymerized condition, by the hot water. Such solutions will, however, lose all their formic aldehyde when the distillation is rapid and is pushed too far. The improved test for methyl alcohol now to be described takes advantage of these facts, and as the procedure not only removes acetaldehyde, but also traces of many other higher boiling substances that exert an injurious influence on the final color reaction, its employment is generally to be preferred to the somewhat simpler method earlier described by us.

When entirely unknown mixtures are under examination they must, of course, always receive in addition a suitable preliminary treatment, though it has been found that a previous digestion with resorcine and acid for the removal of aldehydes, will seldom be required when these substances are not present in larger quantities than are usually found in the distillates from fermented and distilled liquors.

Unless the mixture to be examined, after receiving whatever preliminary treatment may have been found necessary, already contains much water, dilute 2 cc. with water until it measures 6 cc. Treat with the oxidized copper spiral as elsewhere described, six times, cooling the tube with running water after each treatment. Next fit the test-tube, which should have a length of 6–7 inches, with a doubly perforated rubber stopper. One perforation of the stopper is to be fitted with a piece of glass tubing drawn out to a *very fine capillary* whose end is forced down so as nearly to touch the bottom of the tube. Let the wide end of the tube, on which the capillary has been drawn, project an inch above the stopper, and attach to the projecting end a bit of rubber connector which

can be closed by a small screw clamp. Fit the second perforation of the stopper with a bit of glass tubing which is placed in connection with a good water suction-pump capable of giving a vacuum of about 20 mm. Support the test-tube by a clamp, so that it will be two-thirds immersed in water in a beaker maintained at 25°–30°. Partially close the screw clamp and apply gentle suction for a few moments so as thoroughly to saturate the liquid with air. Then screw the clamp tight and apply suction with the full power of the pump. A rapid stream of gas bubbles, at first principally air, but later consisting of acetaldehyde, alcohol, and water vapor, will rise from the fine capillary point, the liquid boiling under the diminished pressure. Continue this distillation *in vacuo* until just one-half of the liquid has evaporated. This requires about ten minutes. By judiciously regulating the action of the pump, and in some cases admitting a very little air through the capillary, the boiling, though accompanied by some frothing, is easily controlled, and bumping prevented.[1] Next add 1 drop of a solution, containing 1 part of resorcine in 200 parts of water to the residual solution, and pour it cautiously into a second tube held in an inclined position in such a way that the two liquids shall not mix. Allow it to stand three minutes; then, holding the tube by its upper end, sway it slowly from side to side in such a manner as to produce a very gentle rotary motion between the two layers. This operation must be persisted in if necessary, for a minute or more, using a piece of white paper for a background; but must be conducted so gently that only a very gradual and partial mixing of the water and acid shall be caused. Nearly half of the acid should remain as a distinct unmixed layer at the end. When methyl alcohol is present, the shaking causes the separation of more or less voluminous flocks of a very characteristic rose-red color. The appearance of colored zones or flocks of other hues, even when tinged with red, or of a rose-red solution without the flocks, should never be considered proof of the presence of methyl alcohol. However, if the flocks are red-

[1] An experienced operator may often obtain equally satisfactory results by simply boiling down the oxidized aqueous solution in an open test-tube until the moment when the odor of acetaldehyde disappears. The method of boiling down *in vacuo* is, however, in general, much more reliable.

dish-brown, or if the upper layer has a pronounced red color, it is often well to repeat the test. Too hasty or careless mixing of the aqueous and acid layers spoils the reaction, which will also fail or give unsatisfactory results if the evaporation *in vacuo* is too long continued, or if it is stopped before the complete removal of all acetaldehyde.

The delicacy of the test as here described is sufficient to permit the detection of 1 part of methyl alcohol in 2000 parts of the solution as prepared for oxidation. If, in a solution of moderate concentration, the proportion of ethyl to methyl alcohol does not exceed 100 parts to 3, entirely satisfactory tests for the latter are obtained without difficulty. When the ratio between the alcohols is 100 : 2, the test is occasionally successful, but cannot be depended upon.

Besides methyl alcohol, the only substances which are known to give the same reaction with the improved resorcine test are the methyl esters and ethers (including methylal), and secondary and butyl alcohols (compounds which are rarely met with except in quantities too small to be readily detected). Acetone and dimethylethyl carbinol give red rings at first, but on shaking, the aqueous layer becomes red-brown without yielding the rose-colored flocks.

As compared with other qualitative tests for methyl alcohol known at the time of writing, the one just presented is without question the simplest, the most rapid, and the most convenient. Its delicacy, while not great, is sufficient for most practical purposes, and its most serious imperfections are so well defined as to be rendered comparatively harmless.

CHEMICAL LABORATORY,
MASS. INST. OF TECHNOLOGY,
August, 1900.

ON SOME DERIVATIVES OF α-NITRO-β-DINITRO-PROPIONIC ALDEHYDE.

BY JOSEPH TORREY, JR., AND OTIS FISHER BLACK.

We have been engaged in a study of the orange-red potassium salt obtained by Hill and Sanger[1] as the principal product of the reaction between mucobromic acid and potassic

[1] Ber. d chem. Ges., 15, 1906 (1882).

nitrite in dilute alcoholic solution, and shown by the same investigators to have the formula $K_2C_3HN_3O_7$.

The investigation has been a difficult one from the start, but the experimental results reached thus far seem to show conclusively that the substance under study is the dipotassium salt of α-nitro-β-dinitropropionic aldehyde; a view which was first suggested by the ease with which the salt passes into what is now known to be potassium nitromalonic aldehyde[1] on heating with water or with dilute alcohol.

In following out this idea it was obviously necessary to establish the presence of an aldehyde group in the molecule, but our first experiments, which were naturally directed to the ordinary aldehyde reactions, were not very satisfactory. Hydroxylamine, though tried under every condition we could devise, yielded us no oxime capable of being isolated; free phenylhydrazine yielded the dihydrazone of nitromalonic aldehyde, while phenylhydrazine hydrochlorate yielded 1-phenyl-4-nitropyrazole. Both these latter bodies have been described by H. B. Hill and one of us,[2] and their appearance here has significance as emphasizing the relationship between the body under study and nitromalonic aldehyde derivatives. With aniline we have had better success. The first results we reached were of the same nature as those just noted in case of phenylhydrazine; *i. e.* we obtained the anil of nitromalonic aldehyde, but we soon found that under different conditions the reaction took a totally different turn, and a careful study of the products obtained in the different reactions has led to results which appear to be decisive.

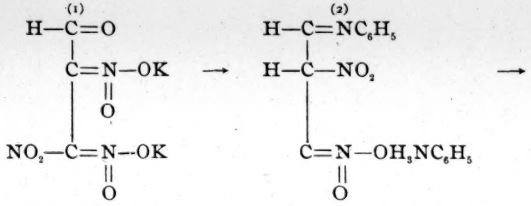
Free aniline has no action upon the potassium salt, either in neutral or alkaline solution; but the aniline salts react readily, and the nature of the reaction is determined by the presence or absence of free strong acid in the solution. In presence of free hydrochloric acid, for example, nitromalonic aldehyde anil is always obtained, but when there is no free strong acid in the solution the reaction takes another course. When the aqueaus solution of the potassium salt is mixed with aniline acetate, or with aniline hydrochlorate in presence

[1] This JOURNAL, **22**, 89 (1899).
[2] *Loc. cit.*

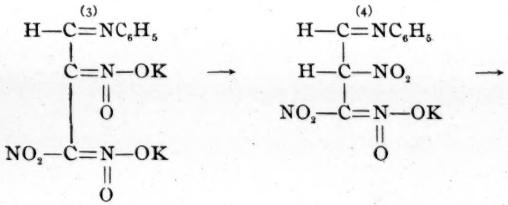
of sodic acetate, a deep yellow substance is precipitated, and this substance, when washed with ether becomes bright lemon-yellow, the ether having washed out a small quantity of a dark-brown oil, which is produced by a side reaction and which causes the slightly darker color of the substance as first precipitated. This bright-yellow substance decomposes at 84°-86° and proves, on analysis, to have the formula $C_{15}H_{15}N_5O_6$. Aqueous potash dissolves it, and on adding alcohol there separates an orange-yellow potassium salt whose formula is $K_2C_9H_6N_4O_6$. Evidently the action of potash upon the yellow substance consists in the elimination of a molecule of aniline, and the replacement of two hydrogen atoms by potassium. On acidifying the aqueous solution of the new potassium salt with any strong acid, there separates a second lemon-yellow substance decomposing at 90° and having the formula $C_9H_8N_4O_6$. The reaction is a perfectly clean one, and consists simply in the replacement of potassium by hydrogen. Finally, on heating the lemon-yellow body with alcoholic potash, there crystallizes out from the cooled solution the original orange-red potassium salt, $K_2C_3HN_3O_7$. In this reaction, then, the phenylimido group has been removed, and its place taken by oxygen, which makes it highly probable that the lemon-yellow substance decomposing at 90° is the anil of the substance $C_3H_3N_3O_7$, which is the free body corresponding to the orange-red potassium salt. Moreover, it will be noticed that the formula of the orange-red salt ($K_2C_3HN_3O_7$) differs from that of the orange-yellow salt ($K_2C_9H_6N_4O_6$) in that in the latter oxygen has been replaced by the phenylimido group; here again the relation is that existing between an aldehyde or a ketone and its anil.

The ready transition to derivatives of nitromalonic aldehyde, together with the formation of an anil, point decidedly to the presence of an aldehyde group in the molecule of the orange-red potassium salt, and also to the presence of a nitro group on the carbon atom adjoining the aldehyde carbon. Furthermore, when the orange-yellow salt is treated, in aqueous solution, with acetic, or even carbonic acid, one atom of potassium is split off, and a monopotassium salt is obtained, a fact which suggests different environment of the two acid hydrogens.

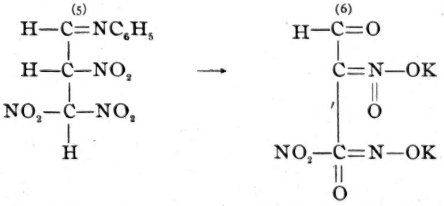
All these facts find a ready explanation in the following formulæ :



Orange-red salt. Body decomposing at 84°–86°.

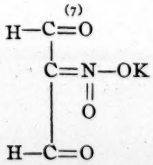


Orange-yellow salt. Monopotassium salt.



Body decomposing at 90° C. Original orange-red salt.

which, heated with water or alcohol, gives :

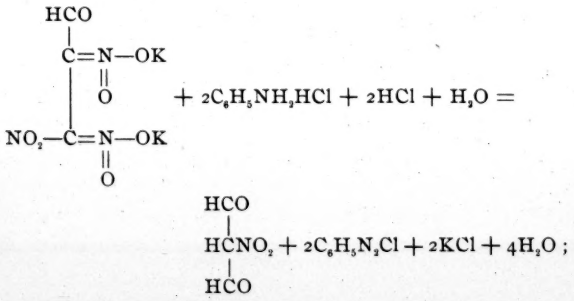


Potassium nitromalonic aldehyde.

According to this view, the orange-red salt is the dipotassium salt of α-nitro-β-dinitropropionic aldehyde.[1] The body obtained by the action of aniline acetate is an aniline salt of α-nitro-β-dinitropropionic aldehyde anil. The orange-yellow salt is the dipotassium salt of α-nitro-β-dinitropropionic aldehyde anil. This, when treated with acid, gives the free anil, which finally yields, on treatment with alcoholic potash, the original orange-red potassium salt of the aldehyde.

These formulæ received unexpected and substantial confirmation when the reaction between the orange-red salt and aniline in presence of strong acids came to be studied more carefully. With 3 molecules of aniline and excess of hydrochloric acid there is a quantitative precipitation of nitromalonic aldehyde anil, and the filtrate contains diazobenzol chloride. By drying and weighing the precipitated anil, and by precipitating the diazobenzol by means of an alkaline solution of β-naphthol, as the nearly insoluble benzol-azo-β-naphthol, we found that for every molecule of the potassium salt present we obtained 1 molecule of nitromalonic aldehyde anil and 2 molecules of diazobenzol.[2]

The elimination of two nitro groups from each molecule of the potassium salt, and the formation of the theoretical quantity of nitromalonic aldehyde anil can only be explained as follows:



$$+ 2C_6H_5NH_2HCl + 2HCl + H_2O =$$

$$+ 2C_6H_5N_2Cl + 2KCl + 4H_2O;$$

[1] Throughout the remainder of this paper the parent substance of the derivatives there described will be called trinitropropionic aldehyde. There is no present danger of any confusion arising.

[2] The yield was, in each case, 91 per cent of the theoretical.

$$\begin{array}{l} HCO \\ | \\ HCNO_2 + C_6H_5NH_2HCl \\ | \\ HCO \end{array} = \begin{array}{l} HCNC_6H_5 \\ | \\ HCNO_2 + HCl + H_2O. \\ | \\ HCO \end{array}$$

Paratoluidine forms derivatives analogous in constitution to those yielded by aniline, and of much the same appearance. Methylamine reacts similarly so far as our studies have extended. These derivatives are described in the sequel.

We have made some attempts to obtain from the potassium salt the free trinitropropionic aldehyde. When the carefully dried potassium salt is brought into a solution of hydrogen chloride in absolute ether, potassic chloride separates and the ether extract yields, on evaporation, a colorless oil having an odor something like that of nitroethane. This oil, on standing for a few minutes at the ordinary temperature, undergoes a sudden and tumultuous decomposition. If treated with alcoholic potash as soon as the ether has evaporated, it yields the original orange-red salt, so it is undoubtedly the free aldehyde, but, owing to its marked instability, we have thus far made no more experiments upon it.

Di-potassium Salt of α-Nitro-β-dinitropropionic Aldehyde (*Dipotassium Trinitropropionic Aldehyde*), $K_2C_3HN_3O_7$.—This body was first described and analyzed by Hill and Sanger in 1882. It is best prepared as follows: Mucobromic acid (20 grams) is dissolved in 70 cc. alcohol, and a saturated aqueous solution of potassic nitrite (26 grams) added. The solution separates into two layers on standing for a minute or two, and water is added in small quantities, with shaking, until the whole becomes homogeneous. In a few moments the action sets in, with effervescence and rise in temperature. The best results are obtained by keeping the mixture at 30°–35°, and the action is over in about half an hour. Considerable of the potassium salt separates in fine orange-red crystals during the last fifteen minutes, and on cooling a further quantity is obtained. The ordinary yield is about 15 grams. The salt is easily purified by solution in water and precipitation with alcohol. As thus prepared, it is very stable under ordinary conditions, and specimens have been kept exposed to the air

for a year without showing any sign of decomposition. It is also stable in slightly alkaline solution, but decomposes in acid solution.

The analyses here given are taken from Hill and Sanger's paper.[1]

	Calculated for $K_2C_3HN_3O_7$.	Found. I.	II.	III.	IV.
C	13.38	13.46	13.68	....	....
H	0.37	0.69	0.68	....	....
N	15.59	15.42	15.81	15.02	....
K	29.05	28.94	28.61	28.80	28.80

Aniline Salt of Trinitropropionic Aldehyde Anil, $C_{15}H_{15}N_5O_6$. —When a water solution of the orange-red salt[2] is mixed with a solution of aniline acetate, or with a solution of aniline hydrochlorate containing excess of sodic acetate, the aniline salt of the anil is precipitated. The best results are obtained when 2 molecules of aniline acetate or hydrochlorate are present for every molecule of the orange-red salt. A very slight excess of acid gives rise to side reactions, the principal product of which is a brownish oil which has not been further studied. The yellow precipitate is well washed with ether, by which means it is obtained pure enough for analysis. We have been unable to find any practicable way of purifying it by crystallization:

I. 0.2178 gram substance gave 0.3925 gram CO_2, and 0.0849 gram H_2O.

II. 0.2117 gram substance gave 0.3855 gram CO_2, and 0.0804 gram H_2O.

III. 0.1795 gram substance gave 30.7 cc. moist nitrogen at 20° and under a pressure of 760.5 mm.

	Calculated for $C_{15}H_{15}N_5O_6$.	Found. I.	II.	III.
C	49.82	49.14	49.67	....
H	4.18	4.33	4.22	....
N	19.44	....	....	19.69

The freshly prepared substance consists of minute lemon-yellow crystals which darken slightly on exposure, though the composition does not seem to alter materially. With acids it

[1] Ber. d. chem. Ges., **15**, 1907.

[2] This method of designating dipotassium trinitroproprionic aldehyde will be followed throughout the present paper.

undergoes an apparently complicated decomposition, one of the products being a diazobenzol salt. The action of alkalies will be described farther on. The crystals are soluble in acetone and somewhat in alcohol, but are nearly insoluble in water and in ether. In the melting-tube they decompose with a puff at 84°-86°.

Dipotassium Trinitropropionic Aldehyde Anil, $K_2C_9H_6N_4O_6.3H_2O$.—When the aniline salt just described is dissolved in cold potassic hydroxide, alcohol precipitates from the solution a red, crystalline substance, which, when dried in the air, takes on a permanent orange-yellow color. The same substance is obtained when trinitropropionic aldehyde anil, soon to be described, is dissolved in alcoholic potash, or, still better, is dissolved in acetone, and the solution precipitated by alcoholic potash. Analysis shows that the substance thus obtained has the formula given above. The material analyzed was purified by solution in water and precipitation with alcohol. The air-dried salt carries 3 molecules of crystal water. One of them is readily given up over concentrated sulphuric acid. The others cannot be determined directly as the temperature at which the water is given off is above the decomposition point of the salt.

I. 0.2702 gram air-dried salt lost 0.0137 gram over H_2SO_4.

II. 0.2565 gram substance dried over H_2SO_4 gave 0.1162 gram K_2SO_4.

III. 0.1880 gram substance dried over H_2SO_4 gave 0.0871 gram K_2SO_4.

	Calculated for $K_2C_9H_6N_4O_6.3H_2O$.	Found.
1 mol H_2O	4.52	5.07

	Calculated for $K_2C_9H_6N_4O_6.2H_2O$.	Found. I.	Found. II.
K	20.56	20.80	20.34

When the anil is used in preparing this salt the yield is quantitative. When the aniline salt is used, the alcoholic filtrate from the potassium salt contains nitromalonic aldehyde dianil, which slowly crystallizes out on standing, in long, silky, yellow needles.

Trinitropropionic Aldehyde Anil, $C_9H_8N_4O_6$.—This substance may be obtained either from its aniline salt or from its potas-

sium salt. When the aniline salt is dissolved in potassic hydroxide and the solution acidified with hydrochloric acid, the anil is precipitated together with some nitromalonic aldehyde anil. A purer product is obtained by dissolving the aniline salt in potassic carbonate, constantly shaking the mixture with a layer of ether, which extracts the liberated aniline. The aqueous solution is then filtered and acidified with hydrochloric acid. The first stage of the reaction consists in the elimination of aniline and formation of the potassium salt of the anil, which, when acidified, gives the free anil. This substance is light-yellow in color and decomposes at 90°. It is soluble in acetone but insoluble in most other common solvents. Heated with alcoholic potash it gives a large yield of dipotassium trinitropropionic aldehyde.

The material used in the following analysis was purified by dissolving it in acetone and adding ligroin, when the anil slowly separates in light-yellow needles :

I. 0.2049 gram substance gave 0.3051 gram CO_2, and 0.0613 gram H_2O.

II. 0.2111 gram substance gave 0.3116 gram CO_2, and 0.0616 gram H_2O.

III. 0.1623 gram substance gave 30 cc. moist nitrogen at 23°.5 and under a pressure of 761 mm.

	Calculated for $C_9H_8N_4O_6$.	Found. I.	II.	III.
C	40.26	40.61	40.26	....
H	3.00	3.25	3.24	....
N	20.94	....	....	20.94

Monopotassium Trinitropropionic Aldehyde Anil, $KC_9H_7N_4O_6$. —When the dipotassium salt of the anil is dissolved in the smallest possible amount of water, and acidified with a weak acid (acetic acid was generally used) a monopotassium salt of the above formula separates in light-yellow crystals.

0.1980 gram substance gave 0.0568 gram K_2SO_4.

	Calculated for $KC_9H_7N_4O_6$.	Found.
K	12.77	12.87

It is much less soluble in water than the normal salt. Treated with hydrochloric acid it gives the free anil ; with alcoholic potash the normal salt is obtained.

Barium Trinitropropionic Aldehyde Anil, $BaC_9H_8N_4O_6.5H_2O$.—This salt is obtained by mixing aqueous solutions of the dipotassium salt of the anil and baric chloride, or by dissolving the free anil in baric hydroxide. It is sparingly soluble in cold water, more so in warm water, and insoluble in alcohol. It may be purified by dissolving it in water at 35°, then cooling and adding alcohol when the pure salt separates in small, red, gleaming plates.

As thus prepared, purified, and air-dried the salt contains 5 molecules of crystal water, of which three are given up over sulphuric acid.

I. 0.2522 gram salt (air-dried) lost 0.0286 gram over H_2SO_4.

II. 0.2236 gram salt, dried over H_2SO_4, gave 0.1173 gram $BaSO_4$.

III. 0.1749 gram salt, dried over H_2SO_4, gave 0.0917 gram $BaSO_4$.

	Calculated for $BaC_9H_8N_4O_6.5H_2O$.	Found.
$3H_2O$	10.92	11.34

	Calculated for $BaC_9H_8N_4O_6.2H_2O$.	Found.	
		II.	III.
Ba	31.18	30.87	30.87

p-Toluidine Salt of Trinitropropionic Aldeyde p-Tolil, $C_{17}H_{19}N_5O_6$.—This substance is very similar in appearance and in properties to the corresponding aniline compound. It can be prepared by adding *p*-toluidine hydrochlorate to an aqueous solution of the orange-red salt, or better, by adding *p*-toluidine hydrochlorate and acetic acid to the dipotassium salt of the *p*-tolil in aqueous solution. As all attempts to recrystallize it resulted unfavorably, it was prepared for analysis by the second of the two methods above mentioned, using as pure material as possible:

0.1977 gram substance gave 0.0896 gram H_2O and 0.3769 gram CO_2.

	Calculated for $C_{17}H_{19}N_5O_6$.	Found.
C	52.38	51.98
H	4.92	5.07

Trinitropropionic Aldehyde p-Tolil, $C_{10}H_{10}N_4O_6$.—By dissolving the *p*-toluidine salt just described in potassic carbonate

and acidifying with hydrochloric acid, the tolil is obtained; but the process is much slower since the separated *p*-toluidine coats the undissolved crystals. By shaking with a layer of ether this difficulty may be partly overcome. The tolil is very similar to the anil and is purified in a similar manner.

I. 0.1903 gram substance gave 0.2954 gram CO_2, and 0.0625 gram H_2O.

II. 0.1664 gram substance gave 29.8 cc. moist nitrogen at 26° and under a pressure of 751.5 mm.

	Calculated for $C_{10}H_{10}N_4O_6$.	Found.
C	42.51	42.33
H	3.57	3.67
N	19.90	19.54

Dipotassium Trinitropropionic Aldehyde-p Tolil, $K_2C_{10}H_8N_4O_6.H_2O$.—This salt is perfectly analogous to the corresponding salt of the anil. It is prepared by adding alcoholic potash to an acetone solution of the *p*-tolil. It is orange-red in color and contains a molecule of crystal water after drying over sulphuric acid.

I. 0.2001 gram salt gave 0.0911 gram K_2SO_4.

II. 0.2473 gram salt gave 0.1127 gram K_2SO_4.

	Calculated for $K_2C_{10}H_8N_4O_6.H_2O$.	Found. I.	II.
K	20.79	20.44	20.41

Monopotassium Trinitropropionic Aldehyde p-Tolil, $KC_{10}H_9N_4O_6$. — The acid properties of the tolil are somewhat weaker than those of the anil. When acetic acid is added to an aqueous solution of the dipotassium salt, the mixture of the monopotassium salt with some free tolil is precipitated. Carbonic dioxide, however, works satisfactorily, and the pure mono salt is obtained. It is yellow in color and is anhydrous.

0.2382 gram salt gave 0.0646 gram K_2SO_4.

	Calculated for $KC_{10}H_9N_4O_6$.	Found.
K	12.22	12.17

Barium Trinitropropionic Aldehyde p-Tolil, $BaC_{10}H_8N_4O_6.4H_2O$.—The *p*-tolil dissolves in baric hydroxide, forming a red solution from which separates a red salt very similar to the barium salt of the anil. The air-dried salt carries 4 mole-

cules of crystal water, of which it gives up three when dried over sulphuric acid.

I. 0.2229 gram air-dried salt lost 0.0250 gram over H_2SO_4.

II. 0.2600 gram air-dried salt lost 0.0279 gram over H_2SO_4.

III. 0.1979 gram salt dried over H_2SO_4 gave 0.1049 gram $BaSO_4$.

IV. 0.2321 gram salt dried over H_2SO_4 gave 0.1237 gram $BaSO_4$.

	Calculated for $BaC_{10}H_8N_4O_8.4H_2O$.	Found. I.	II.
$3H_2O$	11.04	11.21	10.73

	Calculated for $BaC_{10}H_8N_4O_8.H_2O$.	Found. III.	IV.
Ba	31.54	31.19	31.36

Action of Methylamine.

When methylamine hydrochlorate is added to an aqueous solution of the orange-red salt, the hydrochlorate seems to cause decomposition of the potassium salt as a weak acid would do. If, however, the two are mixed in alkaline solution, the monopotassium salt of trinitropropionic aldehyde methylimide is precipitated. We have also obtained the dipotassium salt and the free methyl imide.

Monopotassium Trinitropropionic Aldehyde Methylimide, $KC_4H_5N_4O_6$.—In the preparation of this salt we obtained the best results by suspending the finely powdered orange-red salt in a little ammonia and adding rather more than the calculated quantity of methylamine hydrochlorate. The salt begins to separate after the solution has stood for a few minutes. It is light-yellow, explodes when heated, and is sparingly soluble in water and in alcohol. Specimens have been kept exposed to the air for two years without any perceptible change. For analysis it was crystallized from carefully warmed dilute alcohol.

I. 0.1490 gram salt gave 0.0524 gram K_2SO_4.

II. 0.1440 gram salt gave 0.0506 gram K_2SO_4.

	Calculated for $KC_4H_5N_4O_6$.	Found. I.	II.
K	16.02	15.79	15.78

Dipotassium Dinitropropionic Aldehyde Methylamide, $K_2C_4H_4$-

$N_4O_6.3H_2O$.—When the monopotassium salt is dissolved in potassic hydroxide, alcohol precipitates a bright-yellow, highly crystalline salt. Its analysis showed that it was analogous to the dipotassium salts already mentioned.

I. 0.1948 gram substance (air-dried) gave 0.1000 gram K_2SO_4.

II. 0.1658 gram air-dried salt gave 0.0852 gram CO_2, and 0.0511 gram H_2O.

	Calculated for $K_2C_4H_4N_4O_6.3H_2O$.	Found.
K	23.26	23.04
C	14.27	14.00
H	2.99	3.44

Trinitropropionic Aldehyde Methylimide, $C_4H_6N_4O_6$.—The monopotassium salt above described is the most convenient starting-point in preparing the free imide. A saturated solution of the salt in water is acidified with hydrochloric acid, when the imide separates in snow-white, pearly crystals. It is sparingly soluble in water, very soluble in acetone, and insoluble in ether. It is best purified by solution in acetone and precipitation by ether.

I. 0.1948 gram substance gave 0.1668 gram CO_2, and 0.0513 gram H_2O.

II. 0.1794 gram substance gave 42.6 cc. moist nitrogen at 18° and under a pressure of 755 mm.

	Calculated for $C_4H_6N_4O_6$.	Found. I.	Found. II.
C	23.27	23.35	....
H	2.93	2.94	....
N	27.24	....	27.14

In this paper, as well as in the previous publications of Hill and Torrey on nitromalonic aldehyde, there are recorded a number of cases where the alkali salts of paraffin nitro bodies have yielded the free body on acidification; in fact this has been the rule, to which we have thus far encountered no exception, though the free body has sometimes proved unstable or has undergone condensation on standing. These results are interesting in connection with Nef's work on the constitution of the nitroparaffins. For instance, he has shown[1] that

[1] Ann. Chem. (Liebig), 280, 264 et seq.

when the sodium salts of the primary nitroparaffins are acidified, aldehydes are obtained, ketones being produced in case of secondary nitro bodies.

With sodium nitroethane, 69.7 per cent of the theoretical quantity of acetaldehyde was obtained. Sodium nitromethane yields a very small amount of free nitromethane together with formic aldehyde. According to Nef, the free body passes at once into the aldehyde by intramolecular oxidation, thus:

$$2CH_3—CH=N(=O)—ONa + H_2SO_4 =$$

$$2CH_3—CH=N(=O)—OH + Na_2SO_4;$$

$$2CH_3—CH=N(=O)—OH = 2CH_3CHO + N_2O + H_2O.$$

These facts have played a somewhat important part in the development of Nef's views on the constitution of the alkali salts of the nitroparaffins.

It will be noticed that most of the bodies described in this paper, and in the others to which we have referred, are secondary nitro bodies, and that the only ones carrying a nitro group on a terminal carbon, are trinitropropionic aldehyde, with its anil, *p*-tolil, and methylimide. Furthermore, they are all derivatives of nitroparaffin aldehydes and their condensation-products. Most of them are solids, insoluble or sparingly soluble in water, trinitropropionic aldehyde alone being a liquid. Taken as a whole, they constitute a group of paraffin-nitro bodies of remarkable stability.

As was previously stated, considerable difficulty has been encountered in the details of the investigation; the analytical work, in particular, being often troublesome. It is with pleasure that we acknowledge many valuable and timely suggestions, particularly from Professor H. B. Hill.

OBITUARY.

SIR JOHN BENNET LAWES.

The originator of many of the methods now used in the scientific study of agricultural processes, and the founder of the first experiment station, after which the State Agricultural Experiment Stations were modeled, died recently at the age of eighty-six. Sir John Lawes was educated at Eton and Oxford and showed his interest in chemistry, after leaving college, by fitting up a laboratory in a barn on his estate at Rothamsted, Herts, where he manufactured calomel, on a commercial scale, by a method which had been recently introduced. In 1837 he began to study the action of various substances on growing plants and to compare the relative values of different fertilizing substances. He carried on experiments with ground bone, both fresh and burned, and phosphatic rocks, and was especially impressed with the great increase in the value of the material, as a manure, after it had been partly converted into more soluble compounds by treatment with sulphuric acid. In 1842 he patented the process for treating apatite and other phosphatic minerals with sulphuric acid to produce the superphosphates, a process which has rendered available a large and comparatively cheap supply of the phosphorus necessary for plant growth. His commercial energy led him to establish a number of factories for the manufacture of manures, and later for the preparation of tartaric and citric acids.

He was able to carry on experiments on many problems relating to agricultural science, at the same time that his attention was given to directing his commercial undertakings, through the assistance of Dr. J. H. Gilbert, whose name has been associated with all the work since 1843. The ground devoted to the experimental work, consisting of 40 acres, was divided into small lots upon which the crops were raised in the usual rotation. A careful record of each lot was kept and the reports upon all kinds of problems, which suggested themselves for experimentation, fill more than nine volumes. The value of his work was quickly recognized by the agriculturists of England, who expressed their appreciation of his efforts by building and presenting to him a laboratory to replace the barn, which had long since been outgrown. In order that the work might suffer no interruption at his death, he transferred the experimental grounds and a fund of £100,000 to a board of trustees. His great influence in extending and ad-

vancing the agricultural pursuits and his valuable contributions to science earned for him many honors from societies in his own country and abroad, and in 1882 he was created a baronet. He also directed his attention to raising the condition of the agricultural worker by the example he set in his method of treatment of his people at Rothamsted, where libraries and schools and other sources of improvement were established. J. E. G.

NOTE.

On the Zinc-Copper Couple for Preparing Zinc Ethyl.

Lachman, some time ago, published a method for the preparation of a zinc-copper couple from zinc dust, and has recently given[1] as a reason for the use of his method the difficulty of preparing zinc filings. It may be worth while to call attention to the fact that a very satisfactory and efficient couple may be prepared from Baker & Adamson's zinc, powdered to pass a 30-mesh sieve, and Kahlbaum's reduced copper. Mix 9 parts of the zinc with 1 part of the copper in a small, round-bottomed flask, and close the latter with a cork bearing a small glass tube. Heat gently over a free flame, turning all the time, till the mass becomes gray and loses its luster, but not till there is any sign of fusion. Seal the glass tube and allow to cool. See "Organic Chemistry for the Laboratory," p. 228. W. A. NOYES.

REVIEWS.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. Beckurts (Braunschweig), C. A. Bischoff (Riga), E. F. Dürre (Aachen), J. M. Eder (Wien), P. Friedlaender (Wien), C. Haeussermann (Stuttgart), F. W. Küster (Clansthal), J. Lewkowitsch (London), M. Märcker (Halle), W. Muthmann (München), F. Röhmann (Breslau), herausgegeben von RICHARD MEYER (Braunschweig). IX Jahrgang. 1899. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1900.

It is always a pleasure to welcome a new volume of this valuable publication. It has become indispensable to chemists. Not only can they find in it references to the important articles of the year but they find also interesting introductions to some sections, so that it may be profitably read. Those who do not regularly receive it are advised to subscribe for it at once. I. R.

[1] This JOURNAL, **24**, 31.

EXPERIMENTAL CHEMISTRY. By LYMAN C. NEWELL, PH.D., Instructor in Chemistry at the State Normal School, Lowell, Mass. Boston: D. C. Heath & Co. 1900. 410 pp.

This is a clearly written book and one that is for the most part free of those faults that one commonly meets with in elementary books on chemistry. The author is evidently a good teacher. He thinks logically and expresses himself clearly. Much weight is given to the experimental side of the subject, and quantitative experiments are more numerous than in most similar books. Whether, under the conditions that prevail in our schools, it is possible for the pupils to perform more than a comparatively small part of these experiments is a question that naturally suggests itself. But, of course, the same question suggests itself in connection with every other book of the kind. I. R.

Addition to the Article by George A. König, page 373.

For the generation of hydrogen sulphide I find that 5 per cent sulphuric hydrate is best adapted. If this dilute acid drops at the rate of 6 cc. a minute, a strong current of the gas will be produced. Repeated titrations have shown that an efficiency of 90 per cent can be obtained. The outflow of the spent acid liquid should be in a level with the copper screen at the bottom of the generating tube.

In generating hydrogen gas I use acid of the same strength but I add sufficient platinum tetrachloride to impart a distinct straw-yellow color.

For carbon dioxide I use a 5 per cent solution of hydrogen chloride.